

Biotic enhancement of weathering and surface temperatures on earth since the origin of life

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ABSTRACT

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Assuming steady state of carbon dioxide levels in a “pressure-cooker” atmosphere/ocean system (10–20 bars, near 100 °C) produced by a land weathering sink and volcanic source (BLAG model), an abiotic Earth model for 3.8 Ga requires present biotic enhancements of weathering to be on the order of 100 or greater, consistent with the limit inferred from experimental and field studies. Using a plausible ratio of the present biotic enhancement (from higher plants) to enhancements produced by microbial activity alone, along with models for continental growth and outgassing rates consistent with geologic evidence, we find that computed surface temperatures hover near 20 °C over geologic time, slowly decreasing to present, after a rapid initial decline as a result of microbial colonization of land. Results are consistent with the first possibility for glaciation in the late Archean/early Proterozoic. Useful modeling of climatic evolution, taking into account biotic enhancement of weathering, can now apparently be extended into the Precambrian, assuming operation of the carbonate–silicate buffer.

Introduction

We consider here the implications of biotic enhancement of weathering to the transition on Earth from a lifeless condition to one where the biota begins to play an increasingly significant role in exogenic geochemical cycling and climatic evolution. We calculate surface temperatures from the Archean to the present, assuming a steady state between carbon dioxide sink (weathering of Ca–Mg silicates) and a volcanic source in the carbonate–silicate cycle [Walker et al., 1981 (“WHAK” model); Berner et al., 1983 (“BLAG” model)]. This approach may well be naive, surely neglecting many factors that may influence temperature including astronomical variations, continental drift affecting land distribution, and variations in organic carbon burial through geologic time (see Walker, in press; Kuhn et al., 1989; Marshall et al., 1988; Barron et al., 1989, Kump

and Barron, 1988; Gerald and Dols, 1990). However, we were surprised by just how reasonable the computed temperature history was for this first (or zero!) order model. For plausible biotic enhancement variation arising from evolutionary developments (microbes to higher plants with an associated rhizosphere), computed surface temperatures remain in a narrow range of $20 \pm 10^\circ\text{C}$ for some 3 billion years, after an initial decline as a result of microbial enhancement of weathering, contrary to the contention of Worsley and Nance (1989) that organic carbon burial is needed to stabilize temperatures.

Sagan and Mullen (1972) proposed that the sun’s luminosity was probably low enough to freeze the oceans some 2 billion years ago if the atmospheric composition were the same as now (the “faint young sun paradox”) yet for the last 3.5 billion years the Earth has had liquid oceans, a fact established from the fossil and marine sedi-

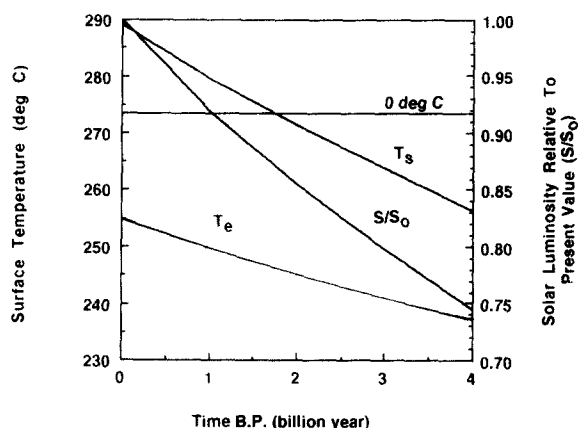


Fig. 1. The Faint Young Sun Paradox. Curve " T_e " is the effective radiating temperature of Earth (constant planetary albedo of 0.3). Curve " T_s " is surface temperature of Earth for constant atmospheric composition (same as now), from Kasting and Ackerman's (1986) climatic model.

mentary record (see Fig. 1). Hence some mechanism for regulation of surface temperature through geologic time is apparently needed. The most likely candidate for this role is the greenhouse gas carbon dioxide. Walker et al. (1981) proposed a negative feedback mechanism for controlling surface temperatures by a steady state level of atmospheric carbon dioxide, achieved by the continental weathering sink and volcanic source.

In the absence of substantial continents, a significant fraction of the present exogenic carbon inventory (on the order of 10 bars) was likely in the atmosphere early in Earth history, having been outgassed during accretion and soon after (Walker, 1985; Kasting and Toon, 1989). More recently, Walker (in press) argues that an initial high level of carbon dioxide is not required because of evidence for a substantial mantle flux now into the atmosphere/ocean. However, we think that the present exogenic inventory is compatible with an initial 10 bar carbon dioxide atmosphere and a substantial mantle flux through time. Impact volatilization of C-type asteroids and comets from 4.5 to 3.8 billion years ago should have supplied a significant fraction of the exogenic carbon inventory (Chyba et al., 1990). We argue that in the absence of biotic enhancement of weathering, just prior to the origin of life, a level of carbon dioxide of some 10 bars is compatible with steady state

conditions given modest continents. We calculate here present biotic enhancements of weathering over abiotic conditions, modeling this steady state at 3.8 Ga.

Kasting (1987) has computed atmospheric carbon dioxide levels necessary to avoid a global ice age in the Archean, while allowing glaciation by the early Proterozoic. He concluded that Archean levels were probably some 100–1000 times the present value, if not higher. Dips in atmospheric carbon dioxide partial pressures are indicated for the late Precambrian and Permian–Carboniferous glaciations and a rise corresponding to the Cretaceous.

Here we give a systematic discussion of the basis for computing surface temperatures on Earth since the origin of life some 4 billion years ago. This modeling uses plausible upper and lower limits on continental area and outgassing rates as a function of time and the best greenhouse function available, taking into account the variation in solar luminosity to compute surface temperatures. We present the results of model calculations going back to the early Precambrian. Tajika and Matsui (1990), in a very innovative paper, have also considered models of the carbonate–silicate geochemical cycle back to the early Precambrian. They calculate the temporal variation of the carbon content of each reservoir assuming constraints on the initial surface carbon, and partitioning of carbonate between continental shelves and ocean floor. They assume a "WHAK" weathering function, i.e., the implicit extension of the present biotic enhancement back to the origin of the Earth. Further reference to their methodology and results will be made in our discussion.

Biotic enhancement of weathering

We have defined the biotic enhancement factor as the ratio of the chemical weathering intensity leading to a carbon sink in the carbonate–silicate geochemical cycle under present conditions to the intensity under abiotic conditions at the same atmospheric carbon dioxide level and surface temperature (Schwartzman and Volk, 1989). In this paper we define this ratio as "B". The conventional view that the biota (read higher plants)

increases chemical weathering rates only slightly was based on a field study in Iceland comparing bicarbonate levels in rivers that drain barren and vegetated areas (Cawley et al., 1969). This study found that weathering rates were at most only 3–5 times higher in the vegetated terrain, an amplification which can probably be accounted for by the elevation of soil partial pressure of carbon dioxide, P_{CO_2} . However, a study by Jackson and Keller (1970) comparing chemical weathering rates of recent Hawaiian lava flows under lichens with those on bare rock found substantially higher biotic amplifications on the order of at least 100 times. Several processes have apparently accelerated weathering under the lichen, including production of organic acids and chelating agents which mobilize essential nutrients for lichen growth, possible elevation of P_{CO_2} and retention of water, producing carbonic acid.

An extensive literature now documents the multifold role of the biota, particularly microbes, in physical and chemical weathering (see recent review in Yatsu, 1988). Physical weathering accelerates chemical weathering by increasing the surface area of minerals exposed to chemical reaction with carbonic acid, oxygen etc. Life apparently acts to accelerate chemical weathering by the following mechanisms:

(1) Microbial decay of organic matter and root respiration raise the carbon dioxide and hence carbonic acid level in soils as previously discussed.

(2) Microbial decay of organic matter in soils also produces organic acids and chelating agents (e.g., oxalic, humic, fulvic and numerous acids produced by lichens) which supply protons and complex with cations, thereby speeding up decomposition of silicates. Many experiments have confirmed this role of microbially produced compounds.

(3) Inorganic acids which attack minerals are produced by sulfur bacteria (sulfuric acid) and nitrifying bacteria (nitric acid).

(4) The biota is itself a sink for soluble products of weathering, including K, Ca, Si, thus according to Le Chatelier's Principle, weathering reactions decomposing silicates are enhanced. Microbes and many higher plants are accumulators of these products (eg., fungi accumulate K, the

horsetail *Equisetum* and grasses accumulate silica). Of course, cations are then made available again to soil solutions upon decay of the organic matter, with a fraction remaining adsorbed and bound to the organics and clay in the soil and subsoil. If the soil mass and biomass are in steady-state, there must be erosion of soil containing these weathering products balancing new soil development. Hence, in relation to the actively decomposing silicates, the biomass is a net sink for soluble products.

(5) Microbes accelerate physical weathering by microfracturing mineral grains. Bacteria and fungi, colonizing rock surfaces, generate polysaccharides which swell when wet, splitting apart mineral grains. The activity of lichens in this regard was demonstrated some 60 years ago. Of course, roots of higher plants contribute significantly to this activity. Moreover the development of microcolonies of bacteria and other microbes in crack systems results in retention of water, allowing the production of carbonic acid.

(6) Soil stabilization by microbes results in cryptogamic soil, while higher plants likewise stabilize soil with their subsurface root system and by the creation of organic litter on the ground, all of which slow down erosion.

(7) Earthworms and other soil fauna are very active in soil formation, increasing porosity, encouraging plant growth, which all accelerate chemical weathering.

The rhizosphere is a creation of the mutual relations between microbes and higher plants. Many of the mechanisms discussed above are amplified by this relationship: e.g., production of oxalic acid by microbial decomposition of leaf litter.

In our opinion, the most important role of biota in accelerating the rate of chemical weathering is the stabilization of soil. A soil, in particular the zone of active decomposition and disintegration of bedrock, greatly increases the chemical weathering of silicates for a given land area because of the high surface area of the mineral grains relative to a bare rock surface. The key role of vegetation in impeding soil erosion is well known from studies around the world. The stabilization effect is not limited to higher plants;

cryptogamic soils found in desert regions are stabilized by algae and lichens (Campbell, 1979; Thornes, 1990). Indeed, the use of off-road vehicles in American deserts breaking up the cryptogamic crust has led to rapid soil erosion. As Campbell (1979) has shown, modern day cryptogamic soils may be models for Precambrian soils, before the emergence of land plants. A sterile land surface for several billion years in the Precambrian is implausible given that prokaryotes stabilize soils today. If this model is correct and a land biota of archaeobacteria and cyanobacteria appeared in the Archean, chemical weathering rates should have been much higher as a result of their soil stabilizing effect.

A recent study on chemical weathering in a soil-free alpine terrain with granitic bedrock (Drever and Hurcomb, 1986) supports the key role of soil in accelerating chemical denudation. Some decomposition of biotite is indicated, with negligible weathering of plagioclase, ordinarily a significant carbon sink, with 60% of the bicarbonate in runoff arising from the reaction of trace amounts of calcite with carbonic acid. We suspect that lichens and algae growing on bare rock may play a significant role in the observed silicate weathering. Further studies of soil-free alpine terrains may contribute to a better understanding of microbial enhancement of weathering.

We believe the weight of evidence supports a value of B on the order of at least 100–1000, with soil stabilization by plants and even microbes (cryptogamic soil) probably being the main factor, although organic complexing and other effects may play an important role. Chemical weathering rates in tropical and temperate soils are at least 1000 times the estimated rate on a bare rock surface at current carbon dioxide levels in the atmosphere with continuous flushing of fresh water (Schwartzman and Volk, 1989). The latter rate, obtained from laboratory experiments, may be one to two orders of magnitude too high because of strain introduced by sample preparation and other effects. Ostwald ripening, the preferential dissolution of smaller grains relative to larger because of the greater surface area per volume of the former (see Steefel and Van Cappellen, 1990), may act, along with erosion from running water and

wind, to smooth out bare rock surfaces, making the 2-dimensional calculation a fair approximation of abiotic conditions. On the other hand, some soil might be present on an abiotic Earth surface, which along with joint systems and aquifers could increase the weathering rate/land area relative to a 2-dimensional bare rock rate. An enhancement factor of 100 is probably a lower limit.

Of course the extrapolation of laboratory dissolution rates of Ca–Mg silicates to field and global scales must be contingent on an understanding of many factors which affect chemical denudation rates including the direct and indirect effects of temperature and partial pressure of carbon dioxide actual reacting mineral surface areas/land area, as well as other phenomena which change as a function of scale. Some recent studies on watersheds have apparently successfully predicted chemical denudation rates from laboratory dissolution data combined with empirical measurements of soil moisture and other parameters (see e.g., Sverdrup and Warfvinge, 1988). The WHAK and BLAG approaches have incorporated temperature and P_{CO_2} factors in their global models based on both laboratory and field data. We have used similar parameterization of these factors (see next section, Eq. 1). We assume, as a first approximation, that factors such as uplift rate which may limit chemical denudation on a large scale are the same for the abiotic and biotic cases.

A model for abiotic to biotic transition on earth

Let $B_0 = W_0/W_{\text{abiotic}}$ where W_0 is the present biotically-enhanced chemical weathering rate and W_{abiotic} is the hypothetical abiotic rate at the same atmospheric carbon dioxide level and surface temperature. Then

$$B_0 / \{ (A/A_0)(V_0/V) \} = (P_{\text{ab}}/P_0)^\alpha e^{(\beta\Delta T)} e^{(\gamma\Delta T)} \quad (1)$$

This formulation adds the biotic enhancement term B_0 to the carbonate–silicate model developed by Walker et al. (1981) and assumes a steady state between carbon sinks and sources with respect to the atmosphere (Schwartzman and Volk,

1989). A_0 , A and V_0 , V are the present and past continental land areas and volcanic outgassing rates (of carbon dioxide) respectively. P_0 is the present atmospheric partial pressure of CO_2 , P_{ab} the partial pressure of CO_2 required under abiotic conditions for steady state, ΔT is the temperature elevation required for an abiotic condition over the present global mean, T_0 , taken as 288 K ($\Delta t = T_{\text{ab}} - T_0$; T_{ab} is the abiotic surface temperature). The factors α , β and γ express the dependence of silicate weathering rate on P_{CO_2} ; temperature and runoff respectively; used $\beta = 0.056$ and $\gamma = 0.017$. Note that $e^{(\gamma\Delta T)} \leq 2$ based on energy considerations (Pollack et al., 1987). We will compute B_0 using Eq. 1, Kasting and Ackerman's (1986) greenhouse relation relating temperature and P_{CO_2} (the variation of solar luminosity is of course included in their model), and models for V and A as a function of time for two possible values of α for $t = 3.8$ Ga, the presumed time of transition from abiotic to biotic conditions.

An age of such transition of 3.8–4 Ga is consistent with the tapering off of intense bombardment of Earth (Maher and Stevenson, 1988) and the first apparent presence of organic carbon in the geologic record (Schidlowski et al., 1983). We assume the following functions for volcanic outgassing, V , and land area, A , variation:

$$V = V_0 e^{(\omega t)}$$

V parallels the decrease in radioactive heat generation in the Earth to present where t is time (age) in billions of years, i.e., the present $t = 0$, $t = 4.55$ at formation of Earth; this formulation is similar to that of Des Marais (1985). We couple the rates of continental land area growth and volcanic outgassing:

$$(dA/dt)_t = -c(dV/dt)_t$$

giving

$$(A/A_0) = (1 + cV_0) - cV_0 e^{(\omega t)}$$

Our rationale for assuming linkage of land area and outgassing rate is that both outgassing of carbon dioxide and continental crust generation are presumably a function of subduction and juvenile outgassing rates. Further, intracrustal growth via underplating results in both outgassing

TABLE 1

Parameters for assumed variation of land area (A) and carbon dioxide outgassing rate (V) as function of age (t)

Model	$(V/V_0)(A_0/A)$ at $t = 3.8$ Ga	cV_0	ω
a ("constant")	$1 \times 1 = 1$	—	0
b ("preferred")	$3 \times 4 = 12$	0.375	0.289
c ("upper limit")	$8 \times 10 = 80$	0.129	0.547

TABLE 2

Definition of symbols

W_0 :	present global biotically-enhanced chemical weathering rate
W_{abiotic} :	hypothetical present global abiotic weathering rate at same atmospheric carbon dioxide level and surface temperature as W_0
B_0 :	= ratio of W_0 to W_{abiotic}
P_{CO_2} :	partial pressure of carbon dioxide
P_0 , P_{ab} :	present atmospheric partial pressure of carbon dioxide, partial pressure required under abiotic conditions for steady state
α :	factor relating to dependence of silicate weathering on atmospheric partial pressure of carbon dioxide
β :	factor relating to dependence of silicate weathering on temperature
γ :	factor relating to dependence of silicate weathering on global runoff
T_0 , T_{ab} ,	present global mean temperature, abiotic
ΔT :	surface temperature, $T_{\text{ab}} - T_0$
V , V_0 :	past and present volcanic outgassing rates of carbon dioxide
A , A_0 :	past and present continental land areas
c , ω :	constants in assumed models of variation of A and V as a function of time
t :	time (age) in billions of years before present
a , b , c :	models for variation of A and V as a function of time (see Table 1)
$V_{\text{effective}}$,	past and present volcanic outgassing rates of
$V_{0,\text{effective}}$:	carbon dioxide corresponding to continental weathering rates at steady state
P_t , T_t :	atmospheric partial pressure of carbon dioxide and temperature under biotically-enhanced conditions
T_e :	effective radiating temperature of the Earth ($^{\circ}\text{K}$) with no greenhouse effect
T_g :	upper global temperature limit for glaciation
B_R :	ratio of present biotic enhancement of weathering factor to past factor, B_0/B_t .

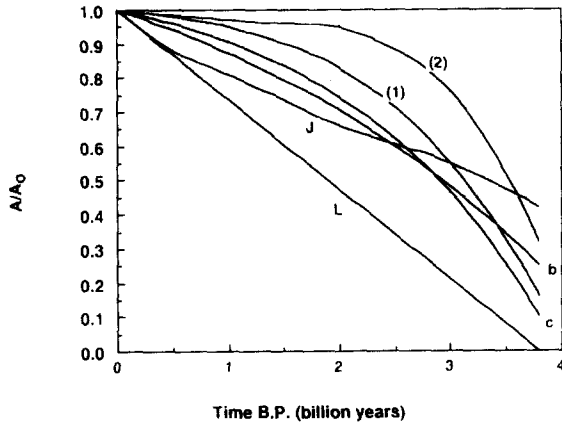


Fig. 2. Growth of continental land area (mass) versus Time; A/A_0 is the ratio of land area at time t to present. Curves b and c correspond to our models b and c respectively, described in text. Curves (1) and (2) are from limiting tectonic/geochemical models of mean age of sediments and continents of Allegre and Jaupart (1985), curve J is from Jacobsen's (1988) inversion of Sm-Nd mass balance for the depleted mantle-continental crust system. Curve L , the linear growth of continental area through time, with $A = 0$ at 3.8 Ga, is taken as a lower limit to A/A_0 as a function of age.

and land area increases through uplift. This parameterization also simplifies model calculations. In any case, an alternative parameterization of land area as a function of time (eg., Allegre and Jaupart, 1985, Jacobsen, 1988; see Fig. 1) consistent with the isotopic evolution of the crust/mantle system, gives similar model results for computed surface temperatures as a function of time (next section).

With the assumptions made above, we constrain the product of outgassing rate and land area ratios, $(V/V_0)(A_0/A)$, at $t = 3.8$ b.y. for two limiting models (models a and c) and a preferred model (b) (Table 1). The variation of A/A_0 , V/V_0 and $(V/V_0)(A_0/A)$ for the above models is shown in Figs. 2–4, respectively. We take the upper limit of the outgassing ratio, V/V_0 , as 8 for the early Archean, approximately 30% higher than an estimate for 3 billion years ago made from a consideration of heat generation rates and depth of eutectic melting and hence source volatile outgassing (Des Marais, 1985). We take a lower limit to land area as 10% of the present value (Allegre and Jaupart, 1985, give values of 16–32% of the present continental mass) and an upper limit to

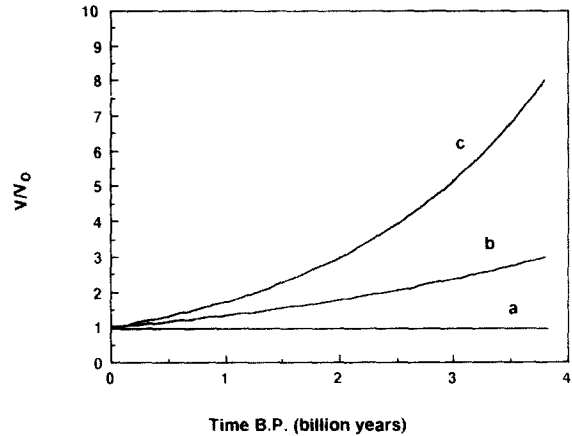


Fig. 3. Carbon outgassing rate relative to present rate (V/V_0) versus time for models a , b and c .

land area as 100% present value. Isotopic dating reveals continental crust in existence at 4–4.3 Ga (Bowring et al., 1989). Armstrong (1968, 1981, 1990) has argued for a constant volume continental crust in existence at least 4 billion years, a model that apparently fits the isotopic data (Nd, Sr, Pb etc.) as well as the net continental growth models. In Armstrong's model, the rate of continental growth equals its rate of destruction in subduction zones. Note that if higher sea-floor spreading rates prevailed in the Archean, sea level should have been higher, thus favoring a lower estimate for land area relative to continental mass than today (Drever et al., 1988).

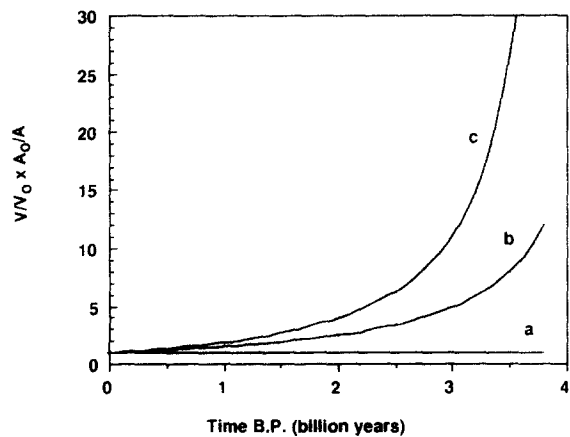


Fig. 4. $(V/V_0) \times (A_0/A)$ versus time for models a , b and c . $(V/V_0) \times (A_0/A)$ for model c at 3.8 Ga (not shown) is 80.

Extreme limits for $(V/V_0)(A_0/A)$ are taken for the assumed values at 3.8 Ga. Model *a* with constant $A = V = 1$ was used to provide a lower limit to $(V/V_0)(A_0/A)$. While a constant or slowly decreasing outgassing rate to present may seem implausible, it is compatible with estimates of the total present exogenic carbon inventory and carbon outgassing fluxes derived from measured $C/{}^3He$ in MORB glasses and 3He outgassing fluxes (Marty and Jambon, 1987; Marty, 1989). This issue will be discussed later at more length in connection with possible non-weathering carbon sinks. To sum up: input parameters for our 3.8 Ga model are the ratios of outgassing rates and land areas, $(V/V_0)_{3.8Ga}$ and $(A_0/A)_{3.8Ga}$ respectively, P_{CO_2} and hence temperature (from Kasting and Ackerman's (1986) greenhouse function), with B_0 , the *present* biotic enhancement of weathering factor, as the output. Three temperatures corresponding to growth conditions for extreme thermophiles were chosen.

Calculations for the 3.8 Ga model give *present* biotic enhancement over abiotic conditions values of $B_0 = 30\text{--}6500$ (preferred model *b* for variation of outgassing and land area: 190–540) and $B_0 = 130\text{--}31,000$ (model *b*: 880–2600) for temperatures of 85 and 110°C respectively for an abiotic Earth surface just at the transition to biotic colonization (Fig. 5). If the Earth's atmosphere at this time contained 10–20 bars of carbon dioxide, surface temperatures could have approached 100°C (Kasting, 1989), the approximate upper temperature limit of thermophilic microbes.

The range of present biotic enhancement of weathering values, B_0 , computed from the 3.8 Ga model is consistent with limits derived from experimental and field studies of weathering, in other words, values of 100–1000 or greater, as discussed above.

We previously outlined a scenario for the colonization of land by extreme thermophiles soon after the origin of life (Schwartzman and Volk, 1989, 1990), leading to the accelerated removal of carbon dioxide via reaction with silicates and drop in temperature since natural selection should have favored those mutants with greater nutrient extraction ability and water retention growth habits. Temperatures for optimal growth of extant ex-

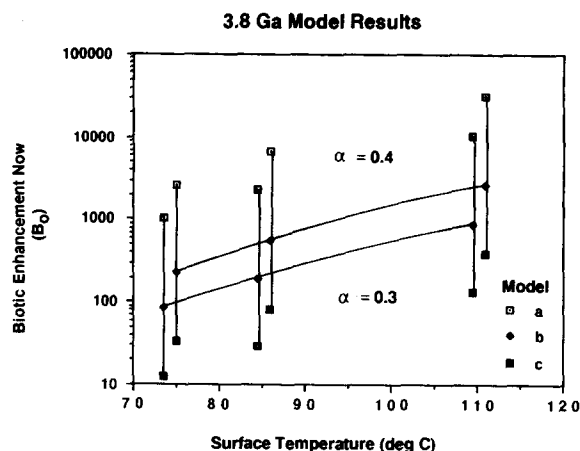


Fig. 5. 3.8 Ga model results: biotic enhancement now versus surface temperature (74, 85 and 110°C). Offset from each temperature was made to separate results from $\alpha = 0.3$ and 0.4; these values of α are derived from experimental data, with $\alpha = 0.4$ the preferred value (see Schwartzman and Volk, 1989).

treme thermophiles range from 74°C (cyanobacteria), through 85°C (methanogens) to 105°C for *Pyrodictium* (upper limit 110°C) (Brock, 1986). Biochemical evidence points to extreme thermophilic eubacteria and archaeobacteria as the most primitive life (Woese, 1987). Thermophilic methanogens, consumers of carbon dioxide and hydrogen, are particularly attractive candidates for the earliest land colonizers. A carbon dioxide-rich atmosphere with hydrogen levels of 1% for 10^8 years is apparently compatible with tropospheric photochemistry (Walker, 1977).

Chemical weathering intensities (fluxes/unit land area) relative to the present rate $\{(V/V_0)(A_0/A)\}$ for the 3.8 Ga model, assuming steady state, range from 1–80 (model *b*: 12). Are these unreasonably high? If the present global physical denudation rate is some 6 times the chemical rate (Holland, 1978), the maximum chemical denudation rate possible at the present mean continental uplift rate is 6 times the present rate. Thus, at 3.8 Ga minimum mean uplift rates of 0.17–13 (model *b*: 2) times present rate are needed for steady state carbon dioxide level in the atmosphere/ocean system. If the mean uplift rates in the early Archean were significantly higher than today's rate (E. Nisbet, pers. comm.) then higher chemical denudation rates would be possible. Alternatively, a steady state was not achieved until later in the

Precambrian, as volcanic emissions declined and land areas increased. Another barrier to achieving steady state was the sheer amount of carbon dioxide in the atmosphere at 3.8 Ga (for 10 bars, most of the carbon dioxide would be in the atmosphere as a result of a low pH ocean; Walker, 1985). The removal time of a 10 bar carbon dioxide atmosphere is estimated to be on the order of 10^8 years computed by dividing an exogenic inventory corresponding to 10 bars (2×10^{21} moles) by $\{(V/V_0)_{3.8\text{Ga}} \times V_0\}$, taking $(V/V_0)_{3.8\text{Ga}} = 3$, V_0 as the volcanic carbon flux (6×10^{12} moles/yr; Berner et al., 1983) to the atmosphere/ocean. Since land area, volcanic outgassing rate and solar luminosity change significantly over 10^8 years, a steady-state approximation is not really justified. However, we stay with the steady-state model for its computational simplicity because our focus is on the role of biotic enhancement of weathering. Transient models have been computed by Tajika and Matsui (1990) and Walker (in press). Thus, our model calculations represent attractors toward which the system is relaxing at any point in time, and not the actual values which could lag behind by several hundred million years. A lag time of this magnitude would apply until the mid-Archean when atmospheric carbon dioxide levels dropped dramatically, making the steady-state model a much better approximation to real behavior (see for example the Phanerozoic model of Berner, 1990a).

These calculations, and those that follow in the next section, assume a balance between a land weathering sink for carbon dioxide and a metamorphic and juvenile outgassing source. We neglect the organic carbon burial sink, which is estimated to have been some 25% of the weathering sink (Berner et al., 1983) from the ratio of the extant kerogen to carbonate reservoirs (also supported by the observed pattern of fractionation of carbon isotopes through time; see Schidlowski et al., 1983). The latter may even be a maximum if carbonates recycle faster than shales (Mackenzie, 1990). Organic carbon burial is irrelevant to abiotic models. As a first approximation, we compute surface temperatures on Earth through the Archean ignoring possible variations in net organic

carbon burial in the past (see next section).

Another carbon sink has been proposed namely the reaction of carbon dioxide with oceanic basaltic crust, particularly in the Archean (Walker, 1983, 1985; Staudigel et al., 1989; Veizer et al., 1989a,b). Nd isotopes in Archean and Proterozoic sediments apparently support the notion that Archean ocean chemistry was dominated by the reaction with basalt, presumably at the ridges (Jacobsen and Pimentel-Klose, 1988a,b; for a contrary view see Alibert and McCulloch, 1990). However, a thermal barrier to subduction of carbonate sediment or reaction product with basaltic crust (Des Marais, 1985) may simply contribute an equivalent volcanic carbon outgassing source to the postulated sink, without affecting geochemical modeling of a land weathering sink balancing a volcanic outgassing source, provided no carbon subduction loss to the mantle has occurred (see Berner, 1990b; Staudigel et al., 1990). If subduction loss of carbon dioxide reaction product with oceanic basaltic crust does occur the V/V_0 ratios assumed in modeling should really be the ratio of carbon dioxide outgassing rates corresponding to the weathering sink alone.

A thermal barrier to carbon subduction loss to the mantle was most likely stronger in the Archean (Abbott and Lyle, 1984; Des Marais, 1985). Several authors postulate subduction loss in the Proterozoic and Phanerozoic (Abbott and Lyle, 1984; Des Marais, 1985; Staudigel et al., 1989). Is subduction loss to the mantle required by plausible extrapolation of present carbon outgassing rates? The present juvenile carbon flux of $2 \pm 0.5 \times 10^{12}$ moles/yr produces the total exogenic inventory (essentially carbonate sediments) in 3.9 billion years which is consistent with a constant flux over time model of outgassing (Marty and Jambon, 1987). However, if the carbon outgassing flux tracked heat generation and oceanic ridge production rates with the outgassing rate ratio, $(V/V_0)_{3.8\text{Ga}}$, significantly greater than about 3, subduction loss to the mantle is required to end up with the present exogenic inventory (Des Marais, 1985; 1989). A calculation of the maximum $(V/V_0)_{3.8\text{Ga}}$ for no requirement of subduction loss to mantle is instructive:

For $(V/V)_{3.8\text{Ga}} = 3$, assuming $V = V_0 e^{(\omega t)}$ as in models *a*, *b*, *c* with $\omega = 0.289$ then

$\Sigma\text{C outgassed}(3.8\text{ Ga} - \text{now})$

$$\begin{aligned} &= V_0 \int_0^{3.8} e^{(\omega t)} dt \\ &= (6.92 \times 10^9)(2 \pm 0.5 \times 10^{12}) \text{ moles} \\ &= 14 \pm 4 \times 10^{21} \text{ moles} \end{aligned}$$

compared to an estimate of the present exogenic inventory of $9 \pm 2 \times 10^{21}$ moles (Marty and Jambon, 1987). However, assuming some 12 bars of carbon dioxide in the atmosphere at 3.8 Ga gives an additional 2×10^{21} moles, with a total predicted present inventory, without subduction loss to mantle, of $16 \pm 4 \times 10^{21}$ moles. Hence, it is possible to have no mantle loss of carbon during subduction with $(V/V_0)_{3.8\text{Ga}} \leq 3$, if the uncertainty in the present exogenic inventory is on the order of 30–50% (Kasting, pers. comm.). A $(V/V_0)_{3.8\text{Ga}} = 3$ assumes a heat generation rate of 4 times present with komatiitic oceanic ridge formation dissipating 30% more heat than basaltic ridge at the same spreading rate (Nisbet, 1987). Note that carbon outgassing rates in the Precambrian up to the Jurassic may have been depressed somewhat compared to the values expected from consideration of heat generation alone, because of the lack of pelagic biogenic carbonate deposition ending up decarbonated in subduction zones (Volk, 1989a). Further, it is possible that no exogenic carbonate reservoir existed 3.8 billion years ago as a result of low pH oceans/rain water. A shift from the contribution to outgassing of juvenile to metamorphic carbon (in subduction zones) from the Precambrian to now would tend to stabilize the flux as a function of time.

Tajika and Matsui (1990) assume that initially all the Earth's carbon (aside from that in the core) was in the surface reservoir, because of the partitioning of carbon between the proto-atmosphere and early magma ocean. Thus, in their model, the degassed carbon during Earth history comes from the release from subducted carbonate and a return flux from a "regassed" component derived from the subducted carbon lost to the mantle. However, since the speciation of carbon in the mantle is not

well understood (SiC may be an important phase according to recent evidence; Leung et al., 1990) it may be premature to conclude that the Earth's early mantle lacked levels of carbon high enough to supply a significant primordial flux through degassing over geologic time. Walker (in press) supports this viewpoint. Further, we think the postulated regassing in the Archean is implausible in view of the apparent thermal barrier (Des Marais, 1985).

If subduction loss of carbon to the mantle, derived from direct reaction of sea water with oceanic basaltic crust, does occur in the Phanerozoic, but not the Precambrian, then $(V_{\text{effective}}/V_{0,\text{effective}}) > (V/V_0)$, since $V_{\text{effective}} = V$ and $V_{0,\text{effective}} < V_0$, where the "effective" V is the carbon dioxide outgassing rate corresponding to the continental weathering sink, and V, V_0 are the total outgassing rates corresponding to the Precambrian and present respectively. Thus, for a given level of biotic enhancement of weathering and land area ratio, (A_0/A) , a bigger value of surface temperature in the past is required than that computed using the model (V/V_0) . If the thermal barrier to subduction loss were not 100% effective in the Archean, then $V_{\text{effective}}$ at that time could be significantly less than V as a result of the apparently substantial uptake of carbonate by the Archean oceanic crust compared to today's crust (Veizer et al., 1989a,b). In this case, $(V_{\text{effective}}/V_{0,\text{effective}})_{\text{Archean}}$ could be less than $(V/V_0)_{\text{Archean}}$ resulting in an opposite effect on computed surface temperatures. In the modeling presented in this paper $V = V_{\text{effective}}$ since only a weathering sink is assumed. Following this definition, we use $(V/V_0)_{3.8\text{Ga}} = 8$ as a limiting case, bearing in mind that subduction loss to the mantle is here required to give the present exogenic carbon inventory even without any carbon sink from the atmosphere/ocean other than continental weathering.

Clearly, a greater understanding of the carbon geodynamic cycle is needed before results from modeling the carbonate-silicate cycle back into the Precambrian can be accepted as definitive. Nevertheless, the model results to be discussed in the next section, based on a weathering sink alone, are strikingly consistent with available geologic data on temperatures (Kasting, 1987) and past

biotic enhancements of weathering relative to today as we will show.

Surface temperatures on Earth since the Early Archean

We now derive an equation for the calculation of past surface temperatures (global mean) for different assumed values of the ratio of biotic enhancements now to that of the past. In general,

$$B_t = (P_{ab}/P_t)^\alpha e^{\beta(T_{ab}-T_t)} e^{\gamma(T_{ab}-T_t)} \quad (2)$$

where B_t is the biotic enhancement at time t , (P_{ab} , T_{ab}) and (P_t , T_t) are the abiotic atmospheric P_{CO_2} and temperature, and biotically-enhanced values respectively, and the reference state here is at time t and not the present as in Eq. (1). Then,

$$B_0/B_t = \left[(A/A_0)(V_0/V)(P_{ab}/P_0)^\alpha \right. \\ \left. \times e^{\beta(T_{ab}-T_0)} e^{\gamma(T_{ab}-T_0)} \right] \\ \times \left[(P_{ab}/P_t)^\alpha e^{\beta(T_{ab}-T_t)} e^{\gamma(T_{ab}-T_t)} \right]^{-1} \quad (3)$$

where the numerator is simply from Eq. 1. Reducing to:

$$B_R = (A/A_0)(V_0/V)(P_t/P_{CO_2}^0)^\alpha \\ \times e^{\beta(T_t-T_0)} e^{\gamma(T_t-T_0)} \quad (4)$$

where $B_R = B_0/B_t$. Recall from the definition of B that $B_0 = W_0/W_{abiotic}$, $B_t = W_t/W_{abiotic}$. The variation of land area and outgassing rate as a function of time follows from models *a*, *b* and *c* given above. Unless otherwise indicated, a value of $\alpha = 0.4$ was used, corresponding to our best estimate of this parameter (Schwartzman and Volk, 1989). The relation between surface temperature T_t and P_{CO_2} is given from a slightly modified greenhouse function from Walker et al., 1981 ($T_0 = 288$ K rather than 285 K, present $T_e = 255$ K rather than 253 K):

$$T = 2T_e + 4.6(P_t/P_{CO_2}^0)^{0.364} - 226.4 \quad (5)$$

where T_e is the effective radiating temperature of the Earth (in K) (no greenhouse effect) at time t .

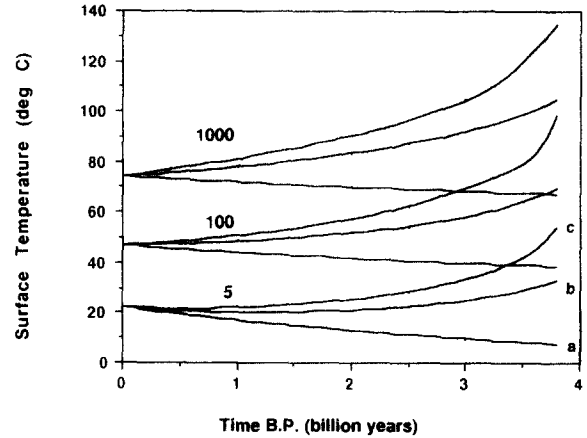


Fig. 6. Computed surface temperatures versus time for models *a*, *b*, *c* (V , A as function of time) for different B_R values (5, 100, 1000). For $B_R = 100$ and 1000, the position of models *a*, *b* and *c* is analogous to that for $B_R = 5$.

We used the following relation for T_e from Kasting (1987):

$$T_e = 255/(1 + 0.087t)^{0.25} \quad (6)$$

where t is time in billion of years before present as already defined. Equation 5 gives similar results to Kasting and Ackerman's (1986) greenhouse function which was not given in equation form (see results in Schwartzman and Volk, 1989). To sum up, our model uses Eqs. 4, 5 and 6 with input parameters being B_R , α , β , γ , and (A/A_0) and (V_0/V) as functions of t , and outputs (P_t/P_0), T_e and T_t .

Computed surface temperatures are shown in Fig. 6. The curves for different ratios of biotic enhancement of weathering now to past factors, B_R , give temperatures for both past biotically-enhanced surfaces (with given B_0/B_t ratios) and abiotic surfaces with $B_0 =$ numerical value of B_R , since Eqs. 1 and 4 are identical in form. First consider the abiotic interpretation. The results simply illustrate our previous conclusion (Schwartzman and Volk, 1989) that an abiotic Earth would be uninhabitable to all but thermophile microbes ($T > 50^\circ C$), were it not for biotic enhancement of weathering with $B_0 > 100$.

Now for the interpretation of temperatures representing past biotically-enhanced Earth surfaces shown in Fig. 6. Note that the temperature record computed for B_R values for biotic conditions

makes no assumptions regarding the actual level of biotic enhancement of weathering over abiotic conditions. The “constant” model *a* results track solar luminosity changes since land area and outgassing rate are constant for this case. For a plausible $B_R = 5$ for much of Earth’s history, it is appears that the “constant” model *a* is inconsistent with the absence of glaciation prior to the early Proterozoic given that temperatures drop progressively back into the Archean (see later discussion). Preferred model *b* gives for $B_R = 5$ temperatures approaching 30°C in the early Archean. An upper bound to temperature variation is given from the upper limit model *c*, largely as a result of rapidly increasing outgassing rates going back in time requiring a higher steady-state atmospheric carbon dioxide level: a total change of some 30°C is indicated for $B_R = 5$. Temperatures appear to be too high to allow for glaciation in the Precambrian.

The sensitivity of computed surface temperatures to the variation of the ratio of outgassing rates, V/V_0 , as a function of time, keeping the same land area variation as in preferred model *b* for the three models, is shown in Fig. 7. The sensitivity of surface temperatures to land area variation, keeping the same outgassing rate variation as in preferred model *b*, is shown in Fig. 8;

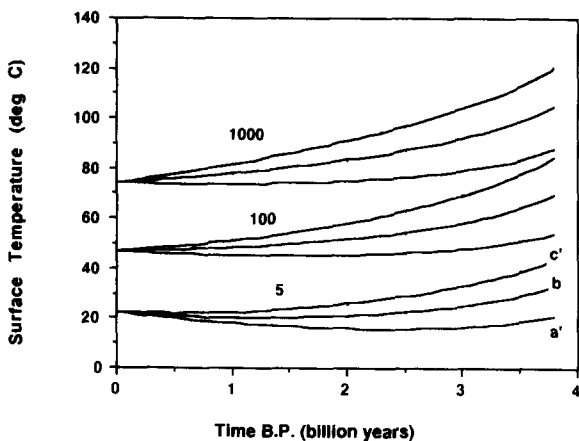


Fig. 7. Computed surface temperatures versus time for models *a'*, *b*, *c'* (for models *a'* and *c'*, V as function of time same as models *a* and *c* respectively) with same A/A_0 variation as model *b*, for different B_R values (5, 100, 1000). For $B_R = 100$ and 1000, the position of models *a'*, *b* and *c'* is analogous to that for $B_R = 5$.

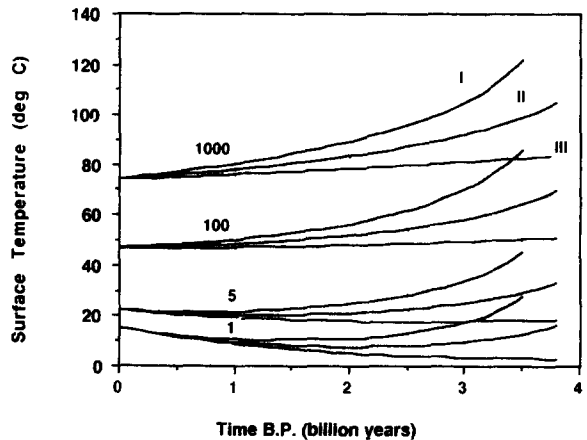


Fig. 8. Computed surface temperatures versus time for models I, II, III (model II is same as *b*, model I assumes a linear variation of A/A_0 as function of time, model III assumes $A/A_0 = 1$ with same V/V_0 variation as model *b*) for different B_R values (1, 5, 100, 1000). For $B_R = 1, 5$ and 100, the position of models I, II and III is analogous to that for $B_R = 1000$.

model *I* assumes a linear growth of A , *II* is the original model *b*, *III* assumes the ratio of land area, $A/A_0 = 1$. Note that the limits on outgassing rate and land area variation produce comparable effects on surface temperature for given B_R values.

Our results for preferred model *b* for land area and outgassing rate variation, with the biotic enhancement ratio, $B_R = 1$, are shown in Fig. 9, along with the computed surface temperatures

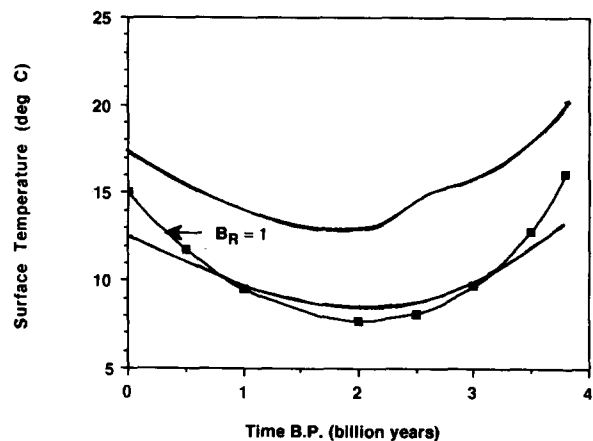


Fig. 9. Computed surface temperatures versus time for model *b* (V, A as function of time) for $B_R = 1$, with upper and lower bounds of model results shown from Tajika and Matsui.

from Tajika and Matsui's (1990) models assuming a similar continental growth function to our preferred model *b*, with variation in the assumed proportion of carbonate accreted on continents and the regassing ratio, with an inferred effective outgassing rate, $V_{\text{effective}}$, variation also similar to our preferred model *b*. Since they also assume a WHAK weathering function, implicitly extrapolating present biotic enhancement back in time, with weathering rates affected by surface temperature and atmospheric P_{CO_2} , it is not surprising that our curve agrees well with their results.

A value of $B_R \equiv 5$ for pre-higher plant land surface weathering is consistent with inferences made from studies on weathering in Hawaii (Jackson and Keller, 1970) and Iceland (Cawley et al., 1969) (see Schwartzman and Volk, 1989, for detailed discussion of these studies). A ratio of present higher plant-enhanced weathering to microbially colonized land of this order (3–10) is indicated from these field studies. This ratio apparently includes a factor resulting from P_{CO_2} elevation in soil (2.5–6 times, using $\alpha = 0.4$) and presence of angiosperms in the present terrestrial ecosystem (global factor of about 2; Volk, 1989b) or the evolution of grasses (J. Robinson, pers. comm.).

We take the onset of the first glaciation on Earth 2.3 billion years ago (the upper limit to the age of the Gowganda formation, 2.24 ± 0.09 Ga, corrected using $\lambda_{\text{Rb},87} = 1.42 \times 10^{-11} \text{ yr}^{-1}$; Fairbairn et al., 1969) to imply the mean surface temperature dropped to the upper temperature limit (" T_g ") of about 20°C for glaciation (Kasting and Toon, 1989). The sensitivity of the computed temperatures to choice of α value at 2.3 Ga is shown in Fig. 10. Note that if the surface temperature was 20°C , 2.3 billion years ago, a B_R of about 4–12 is indicated for "constant" model *a* ($\alpha = 0.3, 0.4$) and preferred model *b* ($\alpha = 0.4$) other choices give B_R less than 3. Kasting and Toon (1989) suggest an uncertainty of "a few degrees" for T_g . If $T_g \leq 25^\circ\text{C}$ values of B_R up to 20 (for model *b*, $\alpha = 0.4$: $B_R \leq 7$) are possible. We conclude the computed range of B_R at 2.3 Ga, assuming surface temperature was 20°C , is consistent with the estimate given above from field studies on contemporary weathering. If the surface

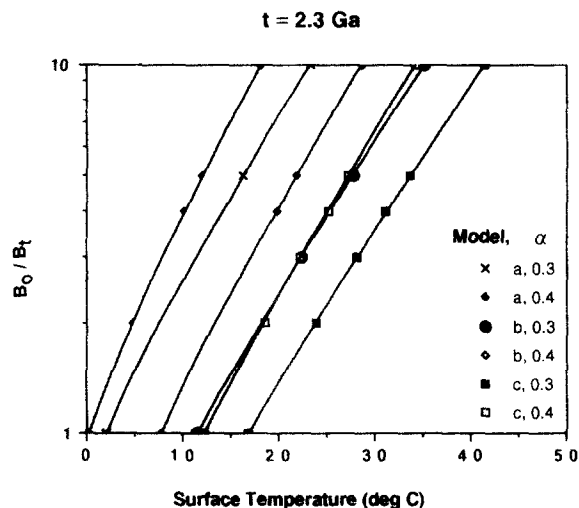


Fig. 10. B_0/B_t versus surface temperature for models *a*, *b* and *c* at 2.3 Ga, the assumed age of the Earth's first glaciation, for $\alpha = 0.3$ and 0.4 .

temperature was 15°C at 2.3 Ga, then rather low biotic enhancements are obtained for preferred model *b* and upper limit model *c*. If preferred model *b* is a good approximation to the actual variation of land area and outgassing rate, this result implies that the biotic enhancement of weathering from higher plants is significantly lower than the present consensus allows.

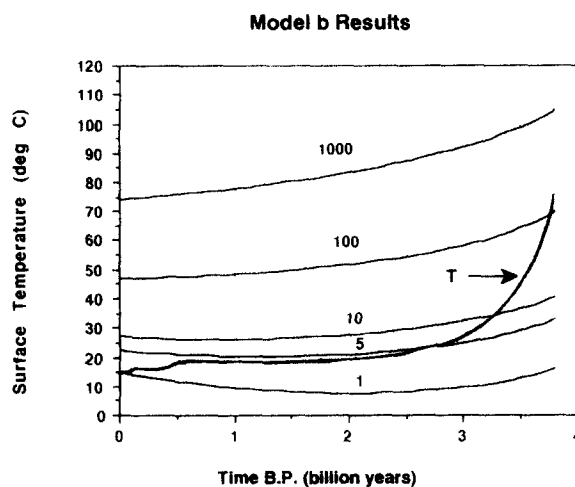


Fig. 11. Computed surface temperatures versus time for model *b* (V_A as function of time) for different B_R values (1, 5, 10, 100, 1000). Our inferred surface temperature history assuming the constraints of this modeling is the hand-drawn curve labeled "*T*".

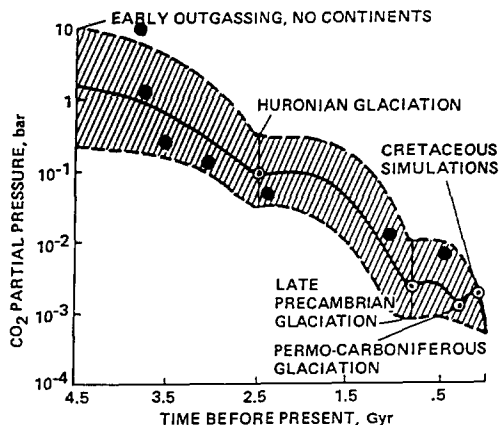


Fig. 12. Atmospheric P_{CO_2} as a function of time from Kasting (1987) with results corresponding to temperature trajectory of Fig. 11 plotted as dots.

Our suggested trajectory of the history of surface temperature, assuming the outlined constraints of the model, is sketched in Fig. 11. We emphasize that this history is a first approximation only to the "real" in that it does not include perturbations in temperature as a result of variations in oceanic carbonate deposition and organic carbon burial, pulses of volcanic outgassing, astronomical factors, continental drift etc. Computed atmospheric carbon dioxide levels fall in the range of Kasting's (1987) estimates even though different greenhouse functions were used (see Fig. 12). Note that a trajectory on this plot simultaneously shows B_R , surface temperature and geologic age. B_R at 3.8 Ga, just before microbes colonized the land, was probably greater than 100 (i.e., weathering rate less than 0.01 times the present value for same P_{CO_2} , temperature) as previously discussed. We postulate an initially rapid decrease in temperature resulting from microbial colonization of the continental surfaces soon after the origin of life as a new steady state carbon dioxide level is achieved in the atmosphere/ocean system. We suggest that rapid evolution of land microbes soon brought on significant biotic enhancement of weathering because of adaptive advantages already mentioned, particularly as a result of soil stabilization. A gradually increasing biotic amplification (*decreasing* B_R), with biotic enhancement of weathering stabilizing at about 0.2 times the present value, corresponding to $B_R \cong 5$) in the Archean resulting

from further evolutionary changes is indicated. Surface temperatures in the early Archean were probably less than 60°C with the presence of gypsum of evaporitic origin limiting $T < 58^\circ\text{C}$ (Walker, 1982). In the Phanerozoic, B_R approaches 1, with "steps" in the temperature curve at 0.4 Ga (first higher plants) and 0.1 Ga (emergence of angiosperms; Volk, 1989b).

Worsley and Nance (1989) inferred that temperatures for the carbonate-silicate buffer acting without coupling to organic carbon would linearly increase from about 15°C , 3.8 billion years ago, to a present value of about 45°C . Our results using plausible biotic enhancement ratios are not consistent with their inferred trend. They only considered the effect of increasing solar luminosity with time, ignoring the counteracting effects of increasing land area and decreasing volcanic outgassing rates. We conclude that their postulated coupling of organic carbon to the carbonate-silicate buffer is not needed to explain the first order temperature record since the Archean; an assumption of steady state created by balancing a weathering sink and volcanic outgassing source is sufficient.

Conclusion

A "pressure-cooker" carbon dioxide-rich model for an abiotic Earth atmosphere some 4 billion years ago is consistent with extreme thermophilic microbes having contributed to the cooling of the Earth's surface in the early Archean. Model calculations for this transition give present biotic enhancement of weathering factors being $\geq 10^2$ for assumed abiotic temperatures greater than or equal to 85°C , factors which from experimental and field inferences are plausible.

First order models balancing the volcanic carbon dioxide source and land weathering sink in the carbonate-silicate geochemical cycle give surface temperatures, Archean to present that are consistent with geologic evidence, particularly the onset of glaciation in the late Archean/early Proterozoic.

These results give some basis for optimism about the possibility of useful modeling of climate evolution back into the Precambrian, based on the assumed operation of the carbonate-silicate

buffer, taking into account biotic enhancement of weathering.

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