Does Life Drive Disequilibrium in the Biosphere?

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Abstract

Lovelock's Gaia hypothesis was born out of his insight that the atmosphere of a lifeless planet would be close to chemical equilibrium, while the robust presence of life would generate measurable disequilibrium. Others have expanded this view to postulate the growing disequilibrium of the Earth's surface system from life's influence over geologic time.

We show that the carbonate-silicate geochemical cycle (Urey reaction), the long-term control on the steady-state atmospheric carbon dioxide level, is far from equilibrium on the present Earth, approaching this state only on a billion-year timescale in the future as solar luminosity and surface temperature climb. Moreover, the progressive increase in the biotic enhancement of chemical weathering in the last 4 billion years, culminating in the weathering regime of the forest and grassland ecosystems, has brought the steady-state atmospheric carbon dioxide level closer to the Urey reaction equilibrium state. In contrast, the abiotic steady state is always further from this equilibrium state than the biotic, except near the origin of life and at their future convergence. These are counterintuitive results from a classical Gaian view.

Equilibrium is an apparent attractor state in biospheric evolution for the case of the Urey reaction and long-term atmospheric carbon dioxide levels, but apparently not for other atmospheric gases, especially oxygen.

Finally, an astrobiological flag: Lovelock's original insight may still be valid for some cases, but far-from-equilibrium abiotic steady states may arise on Earth and other planets, and should not be taken as a priori evidence for Gaian self-regulation.

Introduction

The origin of the Gaia concept is rooted in Lovelock's realization that the Martian atmospheric composition should indicate the presence or absence of an indigenous biota: "If the planet were lifeless, then it would be expected to have an atmosphere determined by physics and chemistry alone, and be close to the chemical equilibrium state. But if the planet bore life, organisms at the surface would be obliged to use the atmosphere as a source of raw materials and a depository for wastes. Such a use of the atmosphere would change its chemical composition. It would depart from equilibrium in a way that would show the presence of life" (Lovelock, 1990, 100). In particular, Lovelock pointed out the coexistence of both oxidizing (oxygen) and reducing (e.g., methane and nitrous oxide) gases in the present Earth's atmosphere.

Lenton (1998, 439) generalized this view: "Lovelock recognized that most organisms shift their physical environment away from equilibrium." Others have gone further, postulating the growing disequilibrium of the Earth's surface system as a result of life's influence over geologic time (see Guerzoni et al., 2001).

First, in considering the merits of these postulates, the departure from chemical equilibrium within the atmosphere should be distinguished from that of the crust/atmosphere interface. This chapter is mainly concerned with testing whether life has tended to bring the crust/atmosphere interface closer to equilibrium than an abiotic regime would. We will return to the proposal that an abiotic atmosphere should be close to equilibrium later. With respect to the crust/atmosphere interface, one should consider the possibility of a purely geochemical nonequilibrium condition of a planetary surface system resulting in steady-state properties, such as atmospheric carbon dioxide level, that are different from chemical equilibrium values.

The long-term carbon cycle ($> 10^5$ years) is controlled by the silicate-carbonate geochemical cycle. This cycle entails transfers of carbon to and from the crust and mantle. Walker et al.'s (1981) geochemical climatic stabilizer is a model of the operation of the silicate-carbonate geochemical cycle first described in the modern era by Urey (1952):

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$CO_2 + CaSiO_3 = CaCO_3 + SiO_2$

The reaction to the right corresponds to chemical weathering of Ca silicates on land ($CaSiO_3$ is a simplified proxy for the diversity of rock-forming CaMg silicates such as plagioclase and pyroxene, which have more complicated formulas (e.g., Ca plagioclase: $CaAl_2Si_2O_8$ and diopside: $CaMg(SiO_3)_2$), while the reaction to the left corresponds to metamorphism (decarbonation) and degassing returning carbon dioxide to the atmosphere. The main aspects of chemical weathering, including the realization that plants are accelerators, and the long-term control mechanism on carbon in the atmosphere were first published over 140 years ago by the French mining engineer Jacques Ebelmen (Berner and Maasch, 1996). It is interesting that Hutchinson (1954), considering the Urey reaction, concluded that several factors on the Earth operate to preclude the likely attainment of an equilibrium level of atmospheric carbon dioxide, but argued that the equilibrium state must account for the general magnitude of the actually occurring level.

Computing the Urey Equilibrium over Geologic Time

We follow up here our previous discussion of this subject based on first approximation calculations of the equilibrium temperature and pCO_2 level, which assumed the classic Urey reaction and no dependence of K on temperature (Schwartzman et al., 1994; Schwartzman, 1999).

Calculation of Effective, Abiotic, and Equilibrium Temperatures

The effective blackbody radiation temperature, T_e, of the Earth was assumed to vary with age (t in Ga) as follows (see Kasting and Grinspoon, 1990):

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

This expression assumes a constant planetary albedo.

Hypothetical abiotic temperatures were computed assuming the biotic enhancement of weathering on the present Earth is 100, thereby subtracting out this biologically mediated cooling effect over the last 4 billion years; the factor of 100 is inferred from field and experimental studies. This model abiotic temperature history was computed from the inferred steady-state levels of atmospheric carbon dioxide over geologic time, controlled by the balance of the weathering sink and volcanic/metamorphic source of carbon dioxide with respect to the atmosphere/ocean reservoir (see Schwartzman and Volk, 1991; Schwartzman, 1999). Equilibrium temperatures and atmospheric pCO_2 levels were computed from thermodynamic data (Faure, 1991; units in kcal/mole) for the Urey-type reactions representing the commonest relevant minerals in the crust and most influential reactions:

(a) $CaCO_3 + SiO_2 = CaSiO_3 + CO_2$

$$\Delta G^o = 9.8, \quad \Delta H^o = 21.28$$

(b) $CaCO_3 + Al_2Si_2O_5(OH)_4$

$$= CaAl_2Si_2O_8 + 2H_2O + CO_2$$

$$\Delta G^o = 8.6, \quad \Delta H^o = 31.2$$

(c) $(CaMg)(CO_3)_2 + 2SiO_2$

$$= CaMg(SiO_3)_2 + 2CO_2$$

$$\Delta G^o = 14.1, \quad \Delta H^o = 37.7$$

K was computed as a function of temperature (T) between 0 and 100°C using the van't Hoff equation:

$$\ln(K_T/K_{298.15}) = -(\Delta H^o/R)[(1/T) - (1/298.15)],$$

$$\text{with } \Delta G^o = -RT \ln K$$

Coupled with a greenhouse function which takes into account the variation in solar luminosity, the temperature and carbon dioxide levels are solvable at any time (i.e., two equations, two unknowns). Only a carbon dioxide/water greenhouse is assumed for simplification, recognizing the possible importance of methane in the Archean/early Proterozoic prior to the rise of atmospheric oxygen (Kasting et al., 2001). We used the greenhouse function given in Caldeira and Kasting (1992) because it gives more plausible temperatures for the low pCO_2 range ($P_t < 0.03$ bar) than the Walker et al. (1981) function (Kasting, personal communication):

$T = T_e + \Delta T$, where T is the mean global surface temperature (°K).

$$\Delta T = 815.17 + (4.895 \times 10^7)T^{-2} - (3.9787 \times 10^5)T^{-1} - 6.7084y^{-2} + 73.221y^{-1} - 30{,}882T^{-1}y^{-1},$$

where $y = \log pCO_2$ (in bars).

For $P_t > 0.03$ bar, an updated version of Kasting and Ackerman's (1986) function, given in equation form by Caldeira (personal communication), with $T_t = f(P_t, S_t)$, where S_t is the relative solar flux at time t:

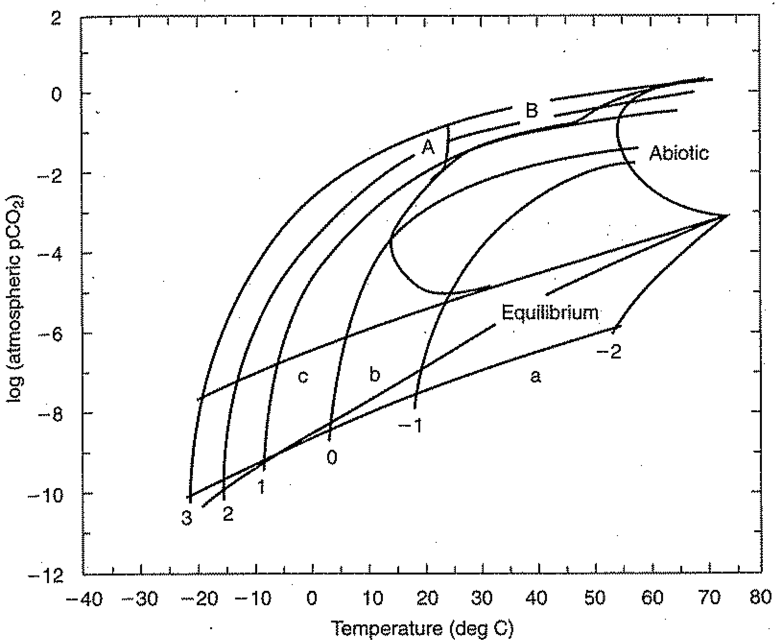

Figure 11.1
Log pCO_2 in atmosphere and surface temperature (deg C) as a function of time for Urey equilibria (labeled a, b, and c, corresponding to same reactions as in text); the surface biosphere (two histories, labeled A and B) and a hypothetical abiotic Earth surface (labeled Abiotic), assuming the present biotic enhancement of weathering is 100. Numbers on curves are in Ga (billion years): positive past, negative future, 0 now.

$$\begin{aligned}T_t = {} & 138.114 - 73.179(p) - 73.960(p^2) + 56.048(p^3)\\ & + 405.836(S_t) + 595.774(p)(S_t)\\ & + 385.004(p^2)(S_t) - 296.420(p^3)(S_t)\\ & - 316.907(S_t^2) - 839.205(p)(S_t^2)\\ & - 548.962(p^2)(S_t^2) + 461.125(p^3)(S_t^2)\\ & + 129.545(S_t^3) + 345.867(p)(S_t^3)\\ & + 251.4629(p^2)(S_t^3) - 216.438(p^3)(S_t^3),\end{aligned}$$

where $p = \log_{10}(P_t/(1\text{ bar})$; the maximum error is 1.95 K; the r.m.s. error is 0.65 K).

The same greenhouse functions were used to compute atmospheric pCO_2 levels corresponding to the surface temperatures in the biotic and abiotic histories shown in figures 11.1 and 11.2.

Results and Discussion

The results are shown in figures 11.1 and 11.2. Two possible temperature and atmospheric pCO_2 histories for the surface biosphere are shown: curves labeled A and B, corresponding to an assumed conventional uniformitarian temperature history and a very warm Archean/early Proterozoic history respectively. Of course curves A and B refer to past and inferred future biotic Earth surfaces. The A curve corresponds to our approximation of the conventional uniformitarian view of past surface temperatures. The B temperature history is argued for in Schwartzman (1999, 2001), with the critical evidence being paleotemperatures derived from the climatic interpretation of the least altered chert oxygen isotopic record. Also plotted in figure 11.2 is the variation of the effective (no greenhouse) temperature as a reference curve. A series of curves labeled "equilibrium" (reactions a, b, and c) show abiotic equilibrium temperatures and corresponding atmospheric carbon dioxide levels, computed as previously outlined. These are hypothetical states which would be achieved only over long times at these relatively low temperatures because of the very slow kinetics of the abiotic solid/gas reaction under these conditions. Sources of the actual disequilibrium at the Earth's surface include the following:

- The steady-state level of atmospheric carbon dioxide is controlled by the balance of the surface weathering sink and the volcanic/metamorphic source from deep subsurface reactions at high temperature and pressure.

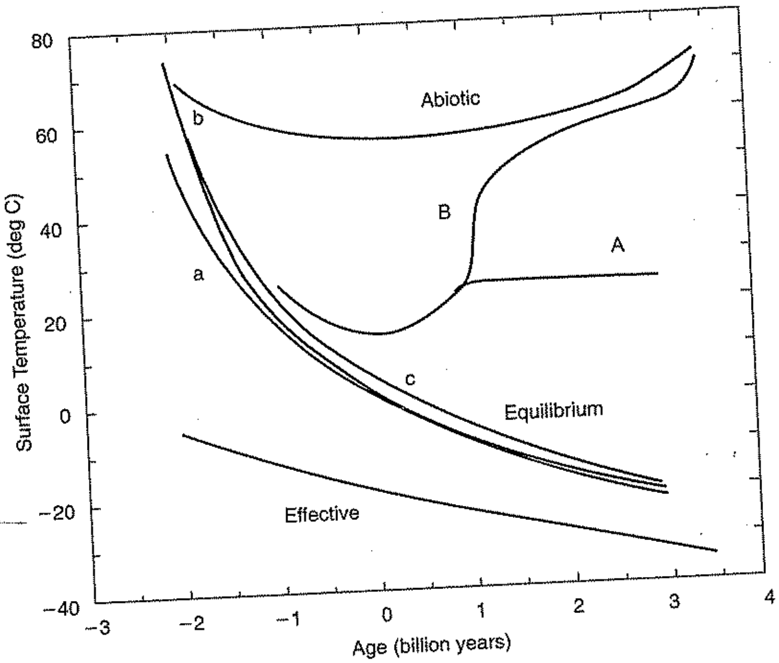

Figure 11.2
Same temperature trajectories as a funtion of age as in figure 11.1. Also plotted is the effective temperature.

- The volcanic/metamorphic source includes a juvenile component of carbon dioxide that is not derived from the reaction of calcium carbonate and silica in subduction zones.

The equilibrium state presumably would be more closely approached in a hypothetical isolated atmosphere/crust system with sufficient carbon dioxide to drive the Urey reaction to the left (reactions a, b, and c given above), exposed calcium silicate, water as a facilitator, and no source of carbon dioxide to the atmosphere other than from surface reaction. Given the slow kinetics of the Urey reaction, disequilibrium is reinforced by the resupply of carbon dioxide to the atmosphere by subduction/metamorphism by virtue of plate tectonics. On the other hand, tectonic uplift provides fresh rock for weathering, which tends to bring the system closer to equilibrium.

The computed results show that the carbonate–silicate geochemical cycle, the long-term control on the steady-state atmospheric carbon dioxide level, is far from equilibrium on the present Earth for both the abiotic and biotic cases, approaching equilibrium only on a billion-year timescale in the future as solar luminosity and surface temperature climb. Steady-state modeling of this geochemical cycle can ignore the equilibrium conditions until their future convergence.

The progressive increase in the biotic enhancement of chemical weathering in the last 4 billion years, culminating in the weathering regime of the forest and grassland ecosystems, has brought the steady-state atmospheric carbon dioxide level closer to the Urey reaction equilibrium state. At present, the equilibrium temperature is about 10°C lower than the actual mean surface temperature, while the corresponding atmospheric pCO_2 level is two to more than four orders of magnitude lower, depending on the equilibrium reaction. For the B scenario, the biotic enhancement of weathering has increased by nearly two orders of magnitude. In contrast, the abiotic steady state is always further from this equilibrium state than the biotic (for both possible temperature histories, A and B), except near the origin of life and at their future convergence. These are counterintuitive results from a classical Gaian view, which argues that life drives its environment away from equilibrium.

On a future Earth both the abiotic and the biotic temperatures will converge on the equilibrium temperature by about 2.5 billion years from now. The increase of solar luminosity overwhelms the regulatory capability of the biosphere, with the carbon dioxide greenhouse effect disappearing. At this point, temperature increases arise from a water greenhouse only, until the hydrosphere is lost. Self-organization of the biosphere here is defined as the increasing influence of life on the structure and physical properties of the Earth's surface. If the biotic enhancement of weathering is now high, and has been rising ever since the origin of life, the self-organization of the biosphere has been geophysiological. Biospheric self-organization has increased with the progressive colonization of the continents and evolutionary developments in the land biota, as a result of surface cooling arising from biotic enhancement of weathering, the equilibrium temperature/pCO_2 of the Urey reaction being the "attractor" state.

With future increase of solar luminosity, and ignoring the possibility of anthropogenic effects, the biospheric capacity for climatic regulation will decrease, leading to the ending of self-organization some 2 billion years from now. The Earth's surface will then approach chemical equilibrium with respect to the carbonate-silicate cycle. If the self-organization of the Earth's surface system is purely geochemical (inorganic), it will likewise end at the same time as the surface temperature converges on the equilibrium temperature. However, there is a possibility that the biotic enhancement of weathering may extend the life span of the biosphere with respect to complex life compared to an abiotic Earth, by delaying the loss of carbon dioxide from the atmosphere (Lenton and von Bloh, 2001).

The biota progressively speeds up weathering from the geologic past to the present, with the surface temperature approaching the equilibrium temperature while the biosphere "self-organizes." Self-organization in the sense previously defined is expressed by the achievement of lower steady-state atmospheric carbon dioxide levels (and therefore surface temperatures) obtaining under biotic conditions than under abiotic, at the same weathering flux at a given time under biotic conditions as abiotic. The key site for this self-organization is at the interface between land and atmosphere, the soil, where carbon is sequestered by its reaction (as carbonic and organic acids) with calcium magnesium silicates. The occurrence of differentiated soil goes back to the Archean, and is the critical material evidence for biospheric self-organization. This biotic invasion into the surface of the continental crust constitutes an ever-expanding front of high surface area/land area with progressive colonization of land and evolutionary developments culminating in the rhizosphere of higher plants. The microenvironments in soils in contact with mycorrhizae and plant roots (the rhizosphere) and microbial biofilms surrounding mineral grains can have significantly higher organic acid and chelating agent concentrations and lower pH than the soil waters commonly sampled (see Berner, 1995; Landeweert et al., 2001). Consider the implications of the estimated surface areas of fungal hyphae, plant roots, and bacteria being 6, 35, and 200 times the area of the Earth, respectively (Volk, 1998). Thus, these biologically created microenvironments probably play an important role in enhancing weathering rates of soil minerals.

Returning to the concept of equilibrium as an "attractor state" for the biosphere, the biotic catalytic role in weathering the crust brings the surface temperature closer to the equilibrium temperature of the Urey reaction. "A fundamental feature of life is its ability to catalyze reactions, and the presence of reactions proceeding at rates faster than predicted for abiotic processes is an indication that life might be present" (Conrad and Nealson, 2001, 20).

Biotic mediation and catalysis of inorganic reactions that are already thermodynamically favorable, such as in supersaturated solutions, brings the affected environment closer to equilibrium. Examples include chemical weathering (e.g., carbonation of silicates and oxidation of crustal Fe^{+2}, Mn^{+2}, and S^{-2}) as well the biologically mediated precipitation of calcium carbonate in the ocean, where surface waters are supersaturated with respect to both calcite and aragonite (Berner, 1971; Holmen, 2000). On the other hand, biologically mediated precipitation may move the environment further from equilibrium, as in the case of modern precipitation of silica in the ocean by diatoms, since surface waters are already undersaturated with respect to amorphous and opaline silica (Berner, 1971). Indeed, the supersaturation of $CaCO_3$ in oceanic surface waters is apparently a partial product of organic inhibition of nucleation (Westbroek and Marin, 2001). As a direct source, the biota may also bring affected environments away from equilibrium (e.g., oxygen rise in atmosphere, carbon dioxide rise in soils). While the rise of oxygen and its steady-state level in the atmosphere undoubtedly require a biotic source, the maintenance of the steady-state level far from equilibrium with respect to surface reduced carbon, especially living matter itself, is a partial outcome of the slow kinetics of surface oxidation (Butcher and Anthony, 2000), as well as of still uncertain biogeochemical feedbacks.

Thus we see that life shoves the environment around in various ways. As in the cases of precipitating $CaCO_3$ from the ocean and chemical weathering, life moves the environment closer to equilibrium. In the cases of precipitating of silica, creating marine

$CaCO_3$ supersaturation, and pumping high oxygen, life moves the environment away from equilibrium. The two cases involving $CaCO_3$ are particularly interesting because life is causing opposite effects within the same chemical system.

In our view, it cannot be said that life is moving the environment toward or away from equilibrium because it has been selected by evolution to do so. Hence we would expect a variety of kinds of effects by life on the environment. The effects on the Gaian (biosphere) scale are best characterized as by-products (Volk, 1998). Were some life to be evolved to actually change the large-scale environment in a certain direction, presumably benefiting from such changes (else why would some life be so evolved?), then cheats that do not perform the environmental manipulation would be at a higher reproductive advantage and soon take over. Oxygen production by plants is a waste by-product. Lowering of CO_2 by weathering is a by-product of mineral gathering, water retention, and microbial respiration, among other factors. In general, Gaia is likely built from environmental effects that are released as free by-products from organisms whose metabolisms evolved for direct benefit to their internal milieu.

Finally, an astrobiological flag: Lovelock's original insight may still be valid for some cases, but far-from-equilibrium abiotic steady states may arise on the surface of Earth and other planets and moons, and should not be taken as a priori evidence for Gaian self-regulation. The future search for alien biospheres will likely include attempts at spectral identification of ozone, indicating the presence of oxygen, and photosynthesis on extrasolar planets (Mariotti et al., 1997). However, the detection of ozone alone may not be conclusive evidence of a biosphere, since traces of oxygen can be generated by abiotic photodissociation of water (see discussion of detection of ozone on two of Saturn's satellites, Noll et al., 1997). One might imagine abiotic sources of methane (e.g., degassing from interior) in atmospheres that also contain such abiotically derived oxygen, thereby generating steady states far from equilibrium.

Thus we cannot simply state that life creates either equilibrium or nonequilibrium as a rule for Gaia or the biosphere. This subject needs more work. In general, we must be careful not to project Earth's example as we look into space for other inhabited worlds. The science of Gaia, applied to astrobiology, needs a new generation of models that can explore simulated planets which, without life, still show disequilibrium. And we need to ask whether certain kinds of life-created equilibria or disequilibria will be more or less probable.

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