

10 Global Relations Between the Redox Cycles of Carbon, Iron, and Sulfur

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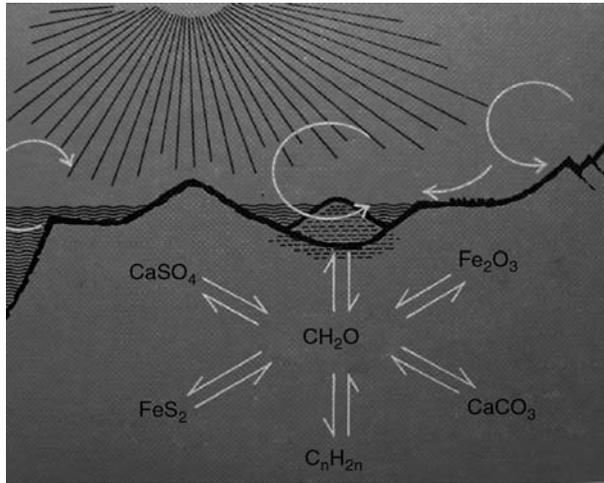
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Abstract: Solar energy has been transformed into useful redox differences or disequilibria within the Earth's crust since the onset of anoxygenic and oxygenic photosynthesis in the Precambrian. Inorganic oxidized carbon is transformed into reduced carbon compounds by capturing and storing solar energy. During this process, many different organic compounds are formed including carbohydrates, proteins, hydrocarbons, and various other complex organic metabolic products and their diagenetic polymerization products (melanin, humic substances, petroleum, coal, and kerogen). Many of these solar energy-enriched compounds, however, are oxidized immediately or during the diagenetic transformation of sediments. The oxidation agents are oxygen, sulfate, iron, and other oxidized compounds, which in turn are partly enriched with the original solar energy. On a global biogeochemical scale, however, sulfur and iron are the most important elements. Geological evidence shows that biogeochemical cycles tend to yield stable ratios between the most oxidized forms of carbon (carbon dioxide and calcium/magnesium carbonate) and the most reduced forms (diamond, coal, methane, and hydrocarbons). Throughout the Earth's history and evolution, this equilibrium ratio is around 1:4, maximally 1:5. When too much carbon is stored in the crust in the form of reduced compounds or vice versa, climatic and biogeomorphogenetic consequences upset the equilibrium. The biosphere reacts in a way to return to the optimal ratio. Excellent examples for this fluctuating equilibrium are the Carboniferous (too much organic carbon stored), the Permian (too little organic carbon stored), and the Tertiary with a generally equivalent production of hydrocarbons and carbonates. At present, we are in a period in which there is a global biogeochemical need to oxidize reduced carbon compounds as fast as possible in order to avoid even more dramatic global climate shifts. The highly evolved human genome seems to be the tool for this shift. Enormous amounts of reduced carbon are turned into the oxidized form as carbon dioxide, which by various biogeochemical pathways is quickly transformed into carbonate, another oxidized form of carbon that can be stabilized and stored in the sedimentary record. Fast recycling of excessively stored solar energy may enable the survival of a global biosphere under highly stressed conditions.

1 Introduction

Since the establishment of life on the Earth, biologically mediated processes gained importance for the evolution of the Earth's crust and upper Mantle. Recently, Falkowski et al. (2008) stated: "Six major elements – H, C, N, O, S, and P – constitute the major building blocks for all biological macromolecules. The biological fluxes of the first five of these elements are driven largely by microbially catalyzed, thermodynamically constrained redox reactions. These involve two coupled half-cells, leading to a linked system of elemental cycles. On geological timescales, resupply of C, S, and P is dependent on tectonics, especially volcanism and rock weathering. However, reversible metabolic pathways in biogeochemical cycles are not necessarily directly related, and sometimes are catalyzed by diverse, multispecies microbial interactions." Several other important elements, however, are incorporated into these biogeochemical cycles. These are Ca, Mg, Fe, Mn, as well as Si in a complex biologically controlled interactive cycling of redox reactions.  *Figure 1* in the communication of Falkowski et al. (2008) clearly outlines the metabolic and energetic relationship between the six major building stones of living matter and the supporting elements.

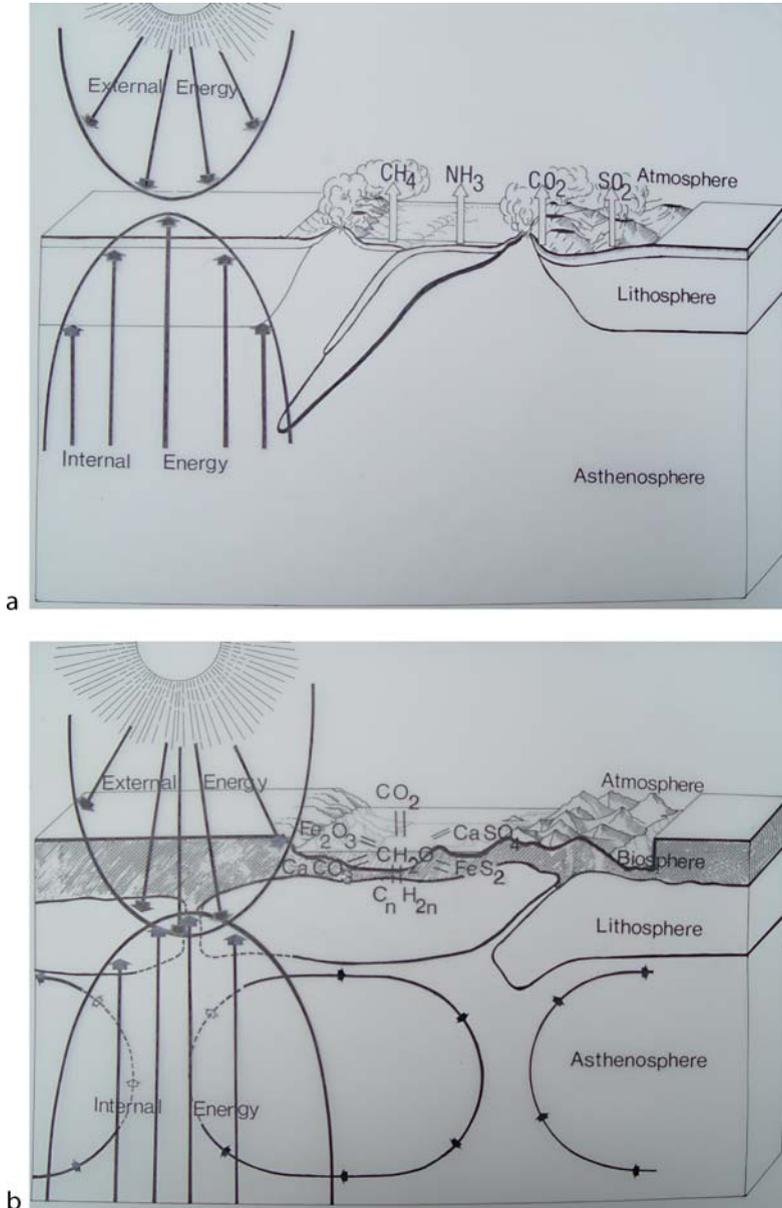
Biological chemosynthesis, anoxygenic and oxygenic photosynthesis, respiration, and disproportioning (fermentation) started and continued to rule the redox status of some



■ **Figure 1**

In subaquatic and subaerial biological systems (including plankton, benthic biofilms, rock biofilms, and symbiotic systems such as lichen, grass, and forests), enormous amounts of solar energy are captured in the form of reduced carbon and sulfur compounds stored in the Earth crust. Parts of these high-energy carbon compounds are transformed by anaerobic respiration (sulfate reduction) into energy-rich iron and other metal sulfides. Biochemical pathways may, however, release some of this geological energy pool and create carbonates, sulfates, and metal oxides poor in chemical energy. Oxygen-rich reduced carbon compounds represent the center of this biological exchange system of atom migration. The buffering reservoir is represented by oxygen-depleted reduced carbon compounds.

major elements of the global geochemical cycles, the most abundant and most important of which are silica and water. The relationship between free oxygen, water, quartz, and silicates is not very well understood. The cycles of carbon, sulfur, and iron have been more thoroughly studied. The role of a mediator or catalyst is played by phosphorus, a rare element always kept in the fully oxidized status and playing the role of a trigger and controller element, which is cycled at enormous speed without ever changing valence. The organic compounds AMP, ADP, and ATP shift phosphorus through biological processes quickly without ever changing its status from oxidized to reduced. The enormous importance of phosphorus can only be matched by the importance of genomes of biological systems controlling the direction and speed of redox processes of the much more abundant elements, carbon, iron, sulfur, calcium (aragonite, calcite), and magnesium (dolomite). The redox status of all elements mentioned is almost exclusively regulated by the capture of solar energy, as postulated at first by Robert Mayer, one of the founders of thermodynamics (Mayer, 1845). He obviously was the first to realize that the atmosphere constantly rejects huge amounts of solar energy in order to avoid overheating. Simultaneously, however, solar energy is captured in biologically controlled amounts to create useful chemical differences or energetic disequilibria, i.e., potential of directed work. Derived from these introductory remarks, we may now envisage a scenario of interaction between reduced and oxidized carbon, iron, and sulfur that includes the most important cations, calcium and magnesium. Phosphorus as a catalyzer was already mentioned as well as the still enigmatic positioning of silica and water



■ **Figure 2**

(a) The young Earth exhibits an oxygen-free atmosphere. Heavy cloud cover and volcanic exhalations through thin crust layers reduce solar heat input to a minimum. Primordial radioactivity and accretion heat reach the surface and keep surface temperatures high. With decreasing internal energy supply, increasing amounts of liquid water and solar luminosity (<30% present levels) minimum life manages to establish itself probably simultaneously in aqueous or terrestrial cooler niches. The chances for the establishment of life probably were highest in polar rocky areas. (b) Solar energy is captured by photosynthesis and stored in the

(including free oxygen) within the framework of biogeochemical cycles, as postulated by Vernadsky (1929).

2 Global Biogeochemistry of Carbon, Sulfur, and Iron

Several elements play an important role in the geochemical cycles of the Earth's crust and upper mantle. Carbon as the key element of life and climate (environmental physical-chemical conditions), iron as enormously rich and important accumulations of minerals in the oxidized form (goethite, hematite), and the reduced form (pyrite), calcium/magnesium in the form of calcium/magnesium carbonates and sulfates, sulfur in the oxidized form of calcium sulfate (anhydrite, gypsum), and in the reduced form as iron (copper, lead, silver, etc.) sulfide.

The interactions among carbon, sulfur, and iron as presented in [Fig. 1](#) are controlled by solar energy input via photophosphorylation and subsequent metabolic cycles of living matter. For example, an increase in the amount of sulfur occurring in the oxidized state as calcium sulfate (anhydrite or gypsum) is accompanied by an increase in the amount of iron occurring in the oxidized state (goethite or hematite). Typical minerals of this interaction between carbon, iron, sulfur, and microbial energy and electron needs are schwertmannite (ideal formula $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$) and jarosite ($(\text{K},\text{NH}_4,\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$), which are cycled by sulfur-oxidizing and sulfur-reducing bacteria. When sulfur turns into the reduced state, also the iron oxides, goethite and hematite, will simultaneously turn into iron and other metal sulfides (e.g., pyrite) (Lovely et al., 2004; Wang et al., 2007). Sulfate is reduced and serves as an electron acceptor liberating carbon dioxide and calcium. These will eventually form calcium and/or magnesium carbonates. Herein direct geological evidence is outlined for the enormous importance of the intimate relationships among carbon, sulfur, and iron. These need to be analyzed on a global scale not only for present-day conditions, but also historically in order to clarify the importance of mass balances for climate and habitability of the Earth in the past and the present. In order to achieve this, one must look at (1) reservoirs (atmosphere, ocean, sediment, crust, and mantle), and (2) residence times and fluxes from a daily scale to geological timescales (Walker, 1993). One must obtain quantitative data on the amounts of energy stored and released through geological time from the reduction and oxidation of iron and sulfur, as related to photosynthesis products, and of geochemical data gained from the analysis of sedimentary systems through geological time (Kasting and Walker, 1993; Krumbein and Schellnhuber, 1992). Further thermodynamics of complex relationships in living ecosystems need to be considered in order to understand how geological timescales are interlinked

form of hydrocarbons, kerogen, and sulfides through partial organic matter oxidation via nitrate, iron, manganese, and sulfate respiration. The resulting sulfides remain as energized reservoirs for future geophysiological activity. Heat storage from above initiates top-down tectonics while internal cooling creates thicker and more stable crustal elements ready for recycling. Disequilibria of these processes are reflected in warm/wet/reduced geological periods (Carboniferous) with excessive reduced carbon production (coal, oil, etc.) and sulfide ores and cold/dry/oxidized periods (Rotliegend/Permian) with excessive production of metal oxides, gypsum, and limestone. The primary and secondary productivity-related ratios of reduced to oxidized carbon, thus, may have oscillated throughout geological periods of time and may have also induced or accelerated ice age periods (near Snowball worlds).

with biological dynamics (Joergensen and Svirezhev, 2004). “Newton’s Laws,” Maxwells law of electricity, Quantum theory, Einstein’s Relativity theories, thermodynamic laws, and laws of radiation need to be incorporated into the analysis of biogeochemical cycles on a geological timescale once they are embedded in biological time. All of them need to be time embedded again into a number of laws covering physical relationships between elements and life as a driving force (Krumbein, 1983; Westbroek, 1991; Gerdes and Krumbein, 1987). From these multiple approaches and assumptions, one may, ultimately, come to the conclusion that not only the intimate relationship between the cycles of carbon, sulfur, and iron is under the control of living systems, but also the dynamics of the Earth itself (Anderson, 1984; Krumbein, 2008). As postulated by Vernadsky (1929), even the migration and close association of all atoms available in the Earth’s crust and upper mantle are accelerated, retarded, or organized in space and time by the force of living matter.

3 Hydrocarbons, Carbohydrates, Limestone, Gypsum, and Pyrite Deposits

How do the cycles of carbon, sulfur, and iron really interact? According to the view of some biogeoscientists (Anderson, 1984; Krumbein, 2008; Rosing et al., 2006), the amount of energy stored in rock deposits is the clue to this question. Photophosphorylation annually captures a certain percentage of solar energy, and transforms it into energy-rich reduced carbon compounds. Only 1% of this production of energy-rich organic compounds is not recycled by annual respiratory activity of the total biosphere and is stored in litter, peat, soil, and sediment organic matter (coal, petroleum, methane, kerogen). This, however, may be sufficient to keep the crust and upper mantle under the control of living matter. This represents only 0.5% of the total mass of the Earth. This uppermost 30–80 km thick and motile layer of rock and magma, however, is most important for biogeochemical and geological cycles and guarantees the survival of a biosphere on the Earth. As Anderson (1984) stated:

- ▶ “It has often been suggested that life established on earth because of a coincidence between the narrow temperature interval over which water is liquid and the temperature extremes that actually occur on earth. The earth apparently is also exceptional in having plate tectonics (or platonic cf. Krumbein, 2008). If the carbon in the atmosphere of Venus could turn into limestone, the surface temperatures and those of the upper mantle would drop. The basalt eclogite phase change would migrate to shallow depths, causing the lower part of the crust to become unstable. Thus there is the interesting possibility that plate tectonics may exist on earth because limestone generating life established itself on this planet.”

On this global and the Earth historical scale, several important facts have apparently been overlooked by modern ecologists and global climate modelers analyzing energy reservoirs, fossil carbon burning, and global climate consequences. These are

1. More than 98% of presently living biomass is represented by microorganisms (bacteria, algae, fungi).
2. More than 99% of the history of life on earth has been organized and controlled by microorganisms (even during the anoxic period??).
3. Cycling (redox reactions using solar energy) has been achieved exclusively by bacterial chemosynthesis and photosynthesis aided very early (beginning in the Precambrian) by

fungal mineralization of reduced carbon compounds and fungal support of photosynthesis through symbiotic cooperation (lichen, plants, trees, forests).

4. Still today in the electric era, more than 99% of all energy transfers and redox reactions are performed by microbes. Examples are sedimentary biofilm, rock biofilm, and continental shelf transformations of oil and methane seepages at global scales exceeding the total energy cycling and waste by human technical manifestations.
5. Microbial life and metabolic activities continue to cycle energy through photosynthetic and respiratory redox reactions keeping the amount of solar energy stored in the Earth's crust relatively constant.
6. Climate and habitability are regulated by biogeochemical and biogeomorphogenetic processes in which the rapid wear-down of subaerial continental surfaces play the same key role as the production of reduced carbon compounds and in turn of oxidized carbonate rocks.

In order to finally underscore these statements, it seems to be appropriate to remind ourselves of the orders of magnitude of these microbial reactions.

4 Global Balance

Kempe (1979) and the *CRC handbook of Chemistry and Physics* through 50 continuous editions give the following amounts for carbon in the Earth's crust. They assume 60×10^{21} g carbonate carbon balanced by 12×10^{21} g organic carbon compounds with a ratio of 5:1–4:1 throughout the geological history. A problem is presented by the different turnover times between 12 years in the biosphere and about 300 million years in the lithosphere. The energetic relations and biogeochemical cycles may be of geological and climate relevance on all time-scales. If we assume an average value of 3,000 kJ free energy for an average organic carbon compound (sugar), we will arrive at values between 15.0×10^{23} and 3.6×10^{24} kJ energy fixed in organic carbon compounds and reduced (sulfide) metal compounds. The annual solar energy capture rate (top-down) in organic carbon compounds and energy-rich sulfides derived from sulfate respiration matches approximately the average annual heat flow of the crust (bottom-up). The most moderate assumption derived from these figures is that solar energy powered organic carbon and sulfide energy budgets and flows in the crust may be of the same order of magnitude as the magma-derived flows powered by the upper mantle of the Earth. In [Figs. 2a](#) and [b](#), an attempt is made to compare a primordial lifeless Earth with little or no mobility of crustal elements with the Earth powered at least partially by captured solar energy with consequent limestone production and mobile and flexible crustal elements, which, in turn, enable nutrient replenishment and climate regulation. Not unlike the rowboat propelled on a thin water layer by human muscle power, flexible plates in the game of continental movements (horizontal and vertical) may be translocated using energies derived from solar power stored in organic carbon compounds and sulfide ores. Hereby, a scenario of a mobile crust and the turnover of elements necessary for living matter is created that matches the early writings of Herder, Kant, and A. von Humboldt (Krumbein and Schellnhuber, 1992; Krumbein, 1996) and the most recent approach of Anderson (2007).

Thus, in a global outlook at the cycles and meeting points of carbon and sulfur, we may need to step forward from biogeochemistry and biogeochemical cycles to geophysiology and a planetary metabolism under the control of living matter and biogenic migration of atoms (Vernadsky, 1929).

An additional view may also be that, in the production and conservation of organic carbon compounds, the sulfur cycle also plays an important role. Pickling of vegetable (cucumber) is an old tradition of making preserves. Pickling again is typical for the production and conservation of hydrocarbons in hypersaline environments. Within the same environments, huge amounts of gypsum and calcium carbonate (limestone) are formed. These in turn are kept sealed by clay minerals produced by climate-derived bioerosion and rock destruction (Gorbushina, 2007). This leads to the accumulation of porous storage rocks capped by impermeable clay layers in the vicinity of oil production sites. Hydrocarbons migrate into these rocks and are covered by huge salt deposits (NaCl, MgCl) and topped by sheet flood-derived clay and silt deposits. Hereby, large differences in the specific weight of rock materials are created facilitating local and global plate or continent movements. Hydrocarbons may, thus, (in connection with gypsum and limestone deposits) also serve as a lubricant not unlike the oil used to keep mobile parts of machines (cars) in constant action.

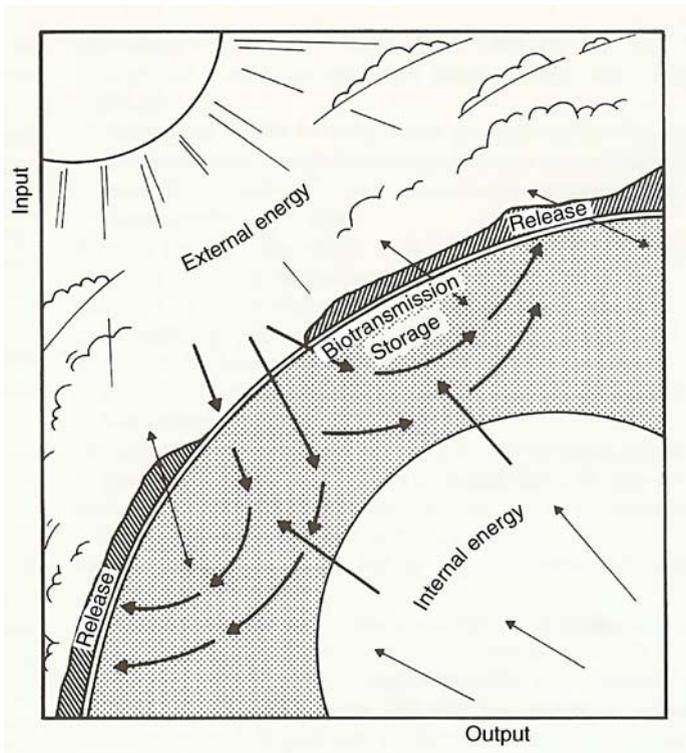
In order to summarize some of the data and thoughts presented so far instead of a discussion or a summary, we put together the step-by-step scenario of carbon, sulfur, iron, and water and silica interactions in a concluding table. The cycles of carbon and sulfur, thus, are intimately

■ **Table 1**

Important geophysiological operations of the bioplanet (Modified from Krumbein and Schellnhuber, 1992)

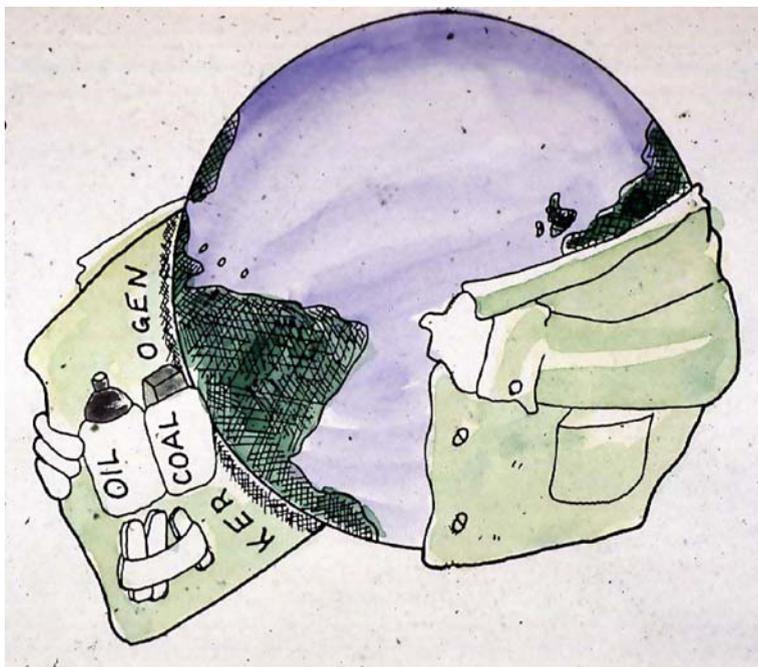
1. Solar-powered anoxygenic and oxygenic photosynthesis creates energy-rich carbon compounds (including 99% kerogen and 1% petroleum and methane)
2. Equilibrated simultaneous production of carbonates (limestone, dolomite)
3. Respiratory and disproportionating (fermentative) action of living matter recycles 99% and deviates some of the energy into energy-rich sulfides. About 1% of the annual production is stored for geological periods of time (carbon and sulfur are at a ratio of 10:1)
4. Living matter controls weathering and solution (oxidation) rates and hereby controls geomorphology via biogeomorphogenesis (Naylor and Viles, 2002)
5. Total control of albedo, i.e., regulation of backscattering of solar radiation by keeping atmospheric composition at relatively constant levels via living matter biogeochemistry
6. Absolute control of phosphorus compounds and their cycling speed by bioenergetics
7. Partial (?) control of the chemical and geomechanical silica and water cycles
8. Speed of biological migration of atoms adapted to external energy stress (changing solar radiation rate)
9. Accelerated mass transfer (horizontal and vertical) via macroorganism evolution
10. Total control of inflow, capture, storage, and release of solar energy via hydrocarbon to carbonate and metal sulfide to metal oxide ratio balancing, powered by photosynthesis, respiration, disproportioning (fermentation), passive (migration), and active transport (swimming, running, flying) of atoms
11. Control on rock densities and atom distribution in atmosphere, hydrosphere, lithosphere, and mantle
12. Bringing carbon, sulfur, and iron cycles under control of living matter (also silica and water?); work needs to be done on this

immediately recycle into water. The amounts of water cycling through the biota, however, may be negligible. Huge amounts of silica are cycled, and again, the biological input into the silica cycle seems to be negligible. On the other hand, the cycles of silica and water seem to have little connection yet to those of carbon, iron, and sulfur in biogeochemical considerations. The deviations of element distribution considering the universe, the whole Earth, and its crust are considerable. If we compare the whole Earth and its crust, only we see major disparities in the following elements (whole earth/crust in percentage). Iron 35/5; oxygen 30/46; silicon 15/27; magnesium 13/2; sulfur 1.9/0.5; calcium 1.1/3.6; and carbon unknown/0.32. Phosphorus and manganese lie in the order of 0.1%. The biologically motivated migration, accumulation, and residence times of all these elements in the Earth's crust are not yet fully analyzed or understood. Seemingly, however, more and more exact data are urgently needed. Long- and short-term consequences of biological cycling of carbon, sulfur, and water are also depicted in a partially humorous way in [Figs. 3–6](#). Most of the data indicated in the *Handbook of Chemistry and Physics* have not been changed since almost 50 years. Most of them have been collected in Institutes of the former Soviet Union Academy



■ **Figure 4**

The relations between external energy, original internal energy, and variable amounts of solar energy stored in sediments and crustal rocks. The amount of stored solar energy varies in different geological eras and formations.



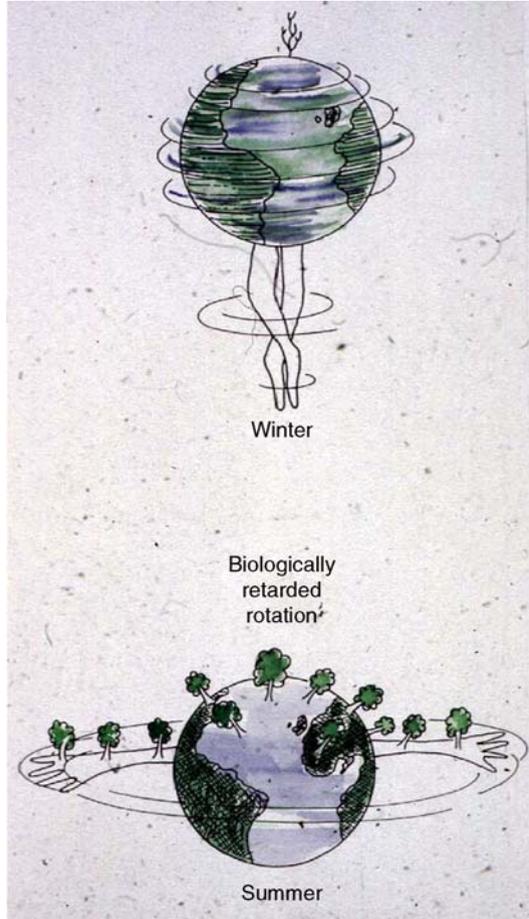
■ Figure 5

A kind of caricature of behavior of a bioplanet on geological scale. Earth is warming, when methane, oil, coal, and kerogen are oxidized and reduced energy-rich carbon compounds are transferred by metabolic oxidation or burning (fire), into the oxidized forms of carbon dioxide and earth alkali carbonates (see Fig. 1). In turn, Earth is cooling, when large amounts of carbon dioxide and calcium carbonate are transformed into reduced energy-rich carbon compounds. The processes seem to be self-regulatory over geological periods of time. The acceleration rate by human activity presently is difficult to assess.

of Science with thousands of mineralogists and geochemists analyzing rocks of different geological periods. We urgently need not only global climate modelers, but also global crustal evolution and dynamic analysts. Fortunately, a new generation of biogeoscientists combining microbiology, geochemistry, and thermodynamics has emerged in the past 30 years since the first Geomicrobiology Chair worldwide was established at Oldenburg University in 1979.

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■ **Figure 6**

Fine tuning of biological impacts has been demonstrated by physicists. The rotational speed of Earth increases on a measurable scale by pumping water several tens of metres up into the foliage of trees and forests in (especially northern) spring and summer and decreases in turn, when the foliage is falling down in fall and winter. Although marginal, the effect is measurable and is an excellent example of global geophysiology on a smaller time scale than production and consumption of reduced carbon compounds over geological periods of time.

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