LIFE AND THERMODYNAMIC ORDERING OF THE EARTH'S SURFACE

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ABSTRACT: A fundamental law of nature states: Natural statistical thermodynamic systems with temperatures greater than 2.7K open to deep space proceed toward states of lower entropy. Entropy reduction can occur by virtue of more entropy (entropy production) being radiated off into deep space. Entropy production is then a measure of the potential of a system to create thermodynamic order. The conversion of low entropy sunlight to high entropy thermal energy reradiated off into space drives the Earth's surface toward lower entropy. By far the most important cause of ordering on the Earth's surface is irradiation by sunlight: The entropy reduction by photosynthesis is probably the main contributer to thermodynamic ordering. Low entropy life has evolved from a high entropy environment. The evolution of life is governed in detail by the trend toward lower entropy or greater biomass. Direct observations show that the entropy of the Earth's surface has, in fact, decreased. Original basalts with solid solutions and small mineral grains or of small-scale order have changed to rocks with large mineral grains or of large-scale order. Elements originally uniformly mixed in the environment now occur segregated into large ore and mineral deposits. The entropy reduction of these processes is numerically estimated.

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1. General Theory

A fundamental law for processes in nature states:

> *Natural statistical thermodynamic systems with temperatures greater than 2.7K open to deep space proceed toward states of lower entropy.*

This law is apparently stated explicitly here for the first time, although it has been used implicitly by cosmologists for many years. It may be readily shown that the law holds on a cosmological scale where the condensation of galaxies, stars (Wesley, 1974a, 1975), and planets involve the conversion of high entropy gas and dust to low entropy matter in celestial bodies. Since the whole is the sum of its parts, what is taking place on a cosmological scale must also be taking place locally. The law must, thus, hold true for all local statistical thermodynamic systems, no matter how small, open to deep space. We are experinecing the local evolution of our star and solar system. The proposed law helps us to describe and understand the long-time irreversible processes we find occurring in nature on the Earth.

The second law of thermodynamics is not violated by the law, because the entropy decrease of the system is smaller (and generally very much smaller) than the increase in entropy of the universe associated with thermal energy of high entropy radiated off into deep space. Since the Earth condensed out of gas and dust thermodynamic ordering processes have continued by virtue of irradiation of the Earth's surface by sunlight. Energy dQ radiated from the sun at a temperature T_s of about 5800K, when absorbed by the Earth's surface is converted to thermal energy of the temperature of the Earth's surface T_e of about 290K. The thermal energy dQ is then reradiated off into deep space. The entropy increase of the universe dS_u, the entropy production, due to this process is then

$$dS_u = dQ(1/T_e - 1/T_s). \tag{1}$$

From the second law of thermodynamics the reduction of the entropy of the Earth's surface $(-dS_e)$ is restricted by

$$(-dS_e) < dS_u. \tag{2}$$

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This result (2) indicates that the entropy production on the Earth's surface dS_u may be regarded as a *potential* to create thermodynamic order; as the greater the right side of Eq. (2), the larger is the *potential* for the left side to be greater. The entropy production, Eq. (1), may also be regarded as a *creation potential*; as no low entropy system can possibly arise or evolve without the entropy production being greater than zero, $dS_u > 0$.

The total entropy production since the earth formed about 4.5×10^9 years ago may be calculated from the total sunlight absorbed and reradiated by the Earth's surface of about 1.5×10^{41} erg (Wesley, 1974b) at the temperature of the Earth $T_e = 290K$ and the radiating temperature of the sun of $T_s = 5800K$. Using Eq. (1) the result is

$$\Delta S(\text{net sunlight on Earth}) = 4.9 \times 10^{38} \text{ erg/K}. \tag{3}$$

This is a measure of the total potential for thermodynamic oder to be created on the Earth's surface due to sunlight. It is a measure of the *likelihood* for thermodynamic order to occur. In a certain sense, the likelihood being so great, it is a measure of the amount of order that is *forced* upon the Earth.

It is of some interest to compare this result (3) with the entropy production associated with the infall energy dissipated to form the Earth from its original cloud of gas and dust. The gravitational energy that has to be dissipated as infall energy in order for the earth to form is given approximately by the gravitational energy of a sphere of uniform density; thus,

$$6GM^2/5r = 4.5 \times 10^{39} \text{ erg}, \tag{4}$$

where G is the universal gravitational constant, M is the mass of the Earth, and r is the radius of the Earth (Wesley, 1974b). The net entropy production is then given by dividing Eq. (4) by the temperature of the original cloud, which, if that of the Earth's surface, yields

$$\Delta S(\text{net infall energy to form Earth}) = 1.6 \times 10^{37} \text{ erg/K}. \tag{5}$$

The infall energy, Eq. (4), was available to create order while the Earth was being formed. This infall energy has still not entirely dissipated. Although some of the Earth's heat arises from radioactive decay, most of the Earth's heat probably remains from the original condensation of the Earth. This internal energy accounts for mountain building, volcanism, tectonics, crustal spreading, and continental drift. The residual or fossil infall energy still produces thermodynamic order in the process of ore and mineral formation. The question then arises as to which is more important in ordering the Earth's surface, solar energy or infall energy. Comparing Eqs. (3) and (5), they might appear more-or-less comparable; but Eq. (5) refers to the potential to order the entire Earth from the center out; while Eq. (4) refers only to the *surface*, which may be approximated as the upper 5 km of the crust. Since the mass of the outer 5 km of the Earth's crust is about 10^{-3} of the mass of the entire earth only about 10^{-3} of the infall potential to create order can be assigned to the surface. Thus, from Eqs. (3) and (5) the ratio of interest becomes

$$\Delta S(\text{infall surface})/\Delta S(\text{sunlight surface}) = 3.3 \times 10^{-5}, \tag{6}$$

The potential to create thermodynamic order on the Earth's surface by infall energy appears to be negligibly small in comparison to the effect of sunlight.

Besides entropy production there is another very important necessary condition for thermodynamic ordering processes to take place. Mechanisms for mass transport must be available. Atoms and molecules must be transported from various places in the environment to a particular site where they can then be organized into an orderly array of low entropy. The mass transport of interest is primarily involved with mechanisms allowing molecular interactions. Low entropy systems of interest are solid systems; so the mass transport must occur in the presence of solids.

2. Life and Entropy Reduction

Life is intimately involved with the thermodynamic ordering processes on the Earth's surface. The low entropy substances comprising life are derived from non-living high entropy precursors in the environment. In this sense the living process is an entropy reducing process. Low entropy life arose or evolved from a high entropy environment. Life tends toward the lowest entropy possible. It may, therefore, be significant that life is mass-wise based upon elements with the lowest entropy and lowest heat capacity C_p, carbon having the lowest, hydrogen the next lowest, and oxygen the fourth lowest. According to Kopp's rule the heat capacity of a compound is given approximately as the sum of the heat capacities of its constituent elements ΣC_{pi}. Using the third law of thermodynamics the entropy S of a compound can then be roughly estimated as the sum of the entropies of its constituent elements S_i; thus,

$$S \approx \sum_i \int_0^T C_{pi}\, d\,ln\, T = \sum_i S_i ,$$

where T is the absolute temperature. A compound composed of elements with lower entropies will, thus, tend itself to have a lower entropy.

Probably the single most important mechanism on the Earth's surface whereby solar energy creates thermodynamic order, or compounds of lower entropy, is provided by living processes. In particular, the all important initial entropy reduction occurs in photosynthesis with the conversion of gaseous carbon dioxide and liquid water into solid carbohydrates and gaseous oxygen; thus,

$$nCO_2 + mH_2O \longrightarrow C_n(H_2O)_m + nO_2 , \qquad (7)$$

where n and m are integers. Considering the inverse process of oxidation of carbohydrates, the process is essentially the oxydation of carbon with the release of energy of 3.33×10^{11} erg/gm of carbon. Since this energy is made available at the environmental temperature of $T = 293K$, the photosynthetic fixation of carbon yields an entropy reduction of about

$$(-\Delta S/\Delta M) = \Delta Q/\Delta MT = 1.14 \times 10^9 \text{ erg/gmK}, \qquad (8)$$

of carbon.

Although the particular process given by Eq. (7) is used for photosynthesis today; it may be assumed that various other processes probably existed in the past to create thermodynamic order under the action of sunlight. Thus, solutions of chemicals, engaging in photosynthetic processes to create thermodynamic order, probably existed from the time of the origin of the Earth. Submicroscopic life may have created order photosynthetically within the first few million years. Microscopic life probably created order photosynthetically over 3×10^9 years ago, leaving no fossil trace. The action of sunlight in providing the *potential* for entropy reduction, Eq. (2), may in a practical sense be regarded as *compelling* or *forcing* ever better entropy reducing mechanisms to arise, thereby finally giving rise to life as it is known today.

The likelihood of life existing elsewhere in the universe has been estimated (Wesley, 1966, 1967, 1974c) using only three *physical* requirements for a favorable environment: 1) the existence of entropy production, 2) the presence of mass transport, and 3) the presence of low entropy solids. From these three criteria it is found that in the solar system the Earth is by far the most favorable place to find life.

3. A Physical Law for the Evolution of Life

The thermodynamic order created by photosynthesis results in: 1) the deposit over geologic time of low entropy permanent detritus, such as limestone, oil, coal, and iron ore and 2) the creation of steady-state low entropy living biomass. The time rate of accumulation of permanent low entropy detritus is very slow, requiring geologic times of the order of millions of years. In comparison the immediate time rate of creation of steady-state low entropy living biomass can be very rapid. The evolution of life is then primarily concerned with the living biomass.

Considering the fundamental law for the direction of natural processes in statistical thermodynamic systems open to deep space and considering the fact that life itself constitutes a portion of the Earth's surface and is itself a statistical thermodynamic system open to deep space, the role of life must be to decrease the entropy of the Earth's surface. Life can reduce the entropy of the Earth's surface by 1) increasing the amount of permanent low entropy detritus or 2) by increasing the steady-state low entropy living biomass. Since life is primarily involved with the immediate creation of living biomass; the following physical law for the evolution of life may be stated (Wesley, 1974d):

> *Life evolves in a direction such as to increase the biomass of the biosphere.*

This physical law for the evolution of life can account for many of the observed evolutionary changes in life in some detail.

Darwin's concept of evolution by natural selection remains valid here. The significant contribution of the present research is to indicate that nature selects the species that tends to provide the greatest biomass for the biosphere. Even within the framework of a sudden environmental stress, such as might arise from a natural catastrophe, the species that can provide the greatest biomass under the physical circumstances will be selected.

The biomass of the Earth has, in fact, increased over geologic times from no life at all when the Earth was first formed 4.5×10^9 years ago to the present-day abundant biomass. The fossil record shows a general increase in the biomass with geologic time from the Cambrian. Ehrensvärd (1962) has estimated that the biomass of the Earth from the Cambrian to the present has increased almost twenty-fold. It is interesting to note that the ecological succession of life on areas following a depletion of life (such as after a forest fire), appearing to recapitulate the primary features of evolution, also reveals an increase in biomass with time.

Although it is often agreed that life does evolve toward a greater biomass, it is generally regarded as having no particular significance. Here, on the contrary, the tendency toward a greater biomass is viewed as the primary driving force for the evolution of life.

To evolve a greater biomass life must necessarily evolve toward greater ecological efficiency. That is, the amount of biomass that can be supported on a given area with a given amount of sunlight, nutriment, or other necessities must increase. It may be seen by direct observation that the more ecologically efficient species tend to dominate. The more efficient species can maintain more individuals over an area to consume the available food or sunlight more rapidly, starving out its less effcient competitors. The more numerous species can also compete more successfully in all ways, other things being equivalent.

To otimize the time-average biomass life must evolve maximal reproduction rates to replace as rapidly as possible biomass temporarily lost, such as during a winter. This explains the remarkably high reproduction rate in practically all species. It may also be appreciated by direct consideration that the species that reproduces the fastest puts more individuals into the field to win over its less numerous competitors.

The proliferation of species evolves, not only to increase the total carrying capacity of an area, i.e., the biomass on the area, but also to establish life in new environments. New life forms that can become established where life was previously absent helps to increase the biomass of the earth.

If phylogenetically primitive species continue to survive, it can only be because they provide the maximum biomass for their niche.

Evolution favors large individual organisms, because generally the ecological efficiency of large organisms is greater than the ecological efficiency of small organisms. The amount of body mass M that can be sustained per unit energy dissipated varies roughly as $M^{1/3}$, since the energy dissipated varies roughly as the surface area or $M^{2/3}$. The fossil record reveals this trend. The largest animal that ever lived is the blue whale, which is living today. The total standing biomass per energy expenditure is to be optimized, which means that the largest species can still become extinct if the ratio $\Sigma n_i M_i / \Sigma n_i M_i^{2/3}$, where n_i is the number of individuals of the ith species, is thereby increased.

It might seem that according to the proposed physical law for evolution that only autotrophs (green plants), decreasing the entropy of the compounds they ingest, should exist on the Earth. Heterotrophs (animals), increasing the entropy of the compounds they consume, would appear to contradict the proposed law. The apparent puzzle is resoved by considering the steady-state situation for the whole biosphere that actually prevails. The compounds in the biomass of heterotrophs also represents a pool of low entropy compounds. For example, the biomass maintained in the ocean is primarily heterotrophs. The evolutionary principle that the biomass increases over geologic time is also applicable to heterotrophs as well as autotrophs. The successful heterotroph is the one that helps to maintain the largest pool of low entropy biomass. Heterotrophs must evolve toward greater ecological efficiency. The evolution of heterotrophs is, thus, ecophysically the same as for autotrophs. In addition, heterotrophs are frequently essential for the survival of autotrophs, such as providing means of fertilization and seed dispersal. In this role heterotrophs may be regarded as nonproductive extensions of autotrophs, like the trunks of trees.

It may be noted that the number of trophic levels and the complexity of ecosystems has generally increased over geologic time. This complex development merely means that organism evolve to take advantage of all possible sources of energy. The significant conclusion is that such complex ecosystems can maintain greater biomass, as is observed.

Territorial behavior of the individuals of a species has evolved to optimally distribute members of the species over an area in order to provide a maximum total biomass for the area.

Since an individual organism is a natural statistical thermodynamic system open to deep space, behavioral patterns have evolved to preserve the low entropy biomass internal to the individual as well as to preserve the biomass of other members of the same species.

4. The Role of Life in Ordering the Earth's Surface

The ordering of the Earth's surface since it condensed out of gas and dust has been essentially powered by sunlight. Both living and nonliving processes have been involved (Meyer, 1985). It is of some interest to investigate the degree of involvement of life in this entropy reduction of the Earth's surface. Life has probably played the predominant role.

The Earth's atmosphere today consists of 20 percent oxygen or 1.1×10^{21} gm of oxygen, which may be regarded as detritus left over from photosynthesis (Meyer, 1985). If this is true, then to release the oxygen about 4.0×10^{20} gm of carbon had to be fixated and deposited as solid detritus on the Earth's surface. Considering the prevalence of CO_2 in the atmosphere of Venus and the prevalence of carbon in the universe, the Earth's atmosphere may have originally contained about 20 percent CO_2. Today the Earth's atmosphere has only a trace of CO_2, 0.00033 parts by mass, left. It would seem that photosynthesis has resulted in essentially all of the original CO_2 being replaced by O_2 in the Earth's atmosphere. The original CO_2 has gone to low entropy permanent detritus, such as limestone, coal, oil, tars, oil shale, etc. From Eq. (8) for the entropy reduction per gram of carbon due to photosynthesis multiplied by the mass of carbon involved of 4×10^{20} gm the total entropy reduction represented by the oxygen in the Earth's atmosphere is

$$\Delta S(\text{carbon to yield } O_2 \text{ in atmosphere}) = - 4.6 \times 10^{29} \text{ erg/K}. \tag{9}$$

The carbon in life on the Earth's surface today acts primarily as a catalyst for entropy reduction. The activity of life on the Earth is essentially cyclic (Wesley, 1974e). Autotrophs take carbon from the air and fixate it as solids on the Earth. Heterotrophs and fires then oxidize this carbon to return it to the air as CO_2. It may be estimated (Wesley, 1974f) that the biosphere fixates on the average about 1.5×10^{17} gm per year. This may be compared with the total biomass and cycled detritus of about 9×10^{17} gm and with the carbon in the atmosphere of 6.4×10^{17} gm and with the carbon in the CO_2 dissolved in the ocean of 1.9×10^{19} gm. Thus, the carbon turn over rate of the total pool of available carbon is about 0.7 percent per year. At this rate in 10^6 years the total pool of carbon of 2×10^{19} gm will turn over about 7×10^3 times. The catalytic action of carbon can, therefore, be tremendous over geologic time.

Life is not involved with carbon, oxygen, and hydrogen alone; it is involved with many elements. These elements are taken up from the solid Earth or from the ocean, generally from the solutions of the salts of these elements. As carbon cycles through the biosphere it necessarily picks up these elements and then necessarily redeposits them in the soil or ocean before passing again into the atmosphere as CO_2. Thus, carbon circulates many elements in the soil and ocean. The turn over rate of these elements in the soil and ocean caused by life can be quite large over geologic times.

Not all of the carbon or other elements associated with life are cycled exactly with 100 percent efficiency. As mentioned above most of the carbon itself was probably removed from the life cycle to become deposited as permanent detritus representing an entropy reduction of the Earth's surface. Other elements are also removed from the life cycle to become deposited as permanent detritus, also with an accompanying entropy reduction of the Earth's surface. One of the most dramatic of these phenomena is the deposition of calcium as calcium carbonate (sometimes kilometers thick) in vast limestone and chalk deposits where the action of life is made evident by the ample presence of fossils. Similarly, iron, copper, zinc, and other elements occurring in life have left the life cycle and have become deposited as permanent detritus over geologic time.

Elements not directly contained in living organisms can also become thermodynamically ordered by virtue of living processes. Life might, for example, leach out preferred elements which are then removed from the original minerals and transported elsewhere. The minerals left behind, being depleted of one or more of their original elements, have a lower entropy. The plentiful occurrence of silicious sand, SiO_2, on the Earth's surface and its absence as an uncombined mineral in the original basaltic type rocks may have arisen by such a process.

It may be readily postulated that by far the most irreversible thermodynamic ordering of the Earth's surface due to sunlight takes place as a consequence of living processes. This postulation is strongly supported by Eq. (6) and the fact that anywhere on the Earth's surface, which is irradiated by sunlight and where mass transport mechanisms on the molecular level are available, life is found. This simply means that wherever the environment is suitable for thermodynamic ordering processes to take place, by whatever means, life is found there (Meyer, 1985). Even if nonliving ordering processes do take place in favorable environments by the direct action of sunlight, they must be relatively unimportant; as life preempts the available sunlight, thereby creating most of the thermodynamic ordering.

It is of interest to note that some life is creating thermodynamic order on the

Earth today using fossil or residual infall energy. This complex advanced life with numerous species is concentrated around deep-sea vents at sea floor spreading centers (Jannasch, 1984). No sunlight penetrates to these depths. Apparently its immediate source of high utility energy is H_2S outgassing from the Earth's mantle. Mass-wise this thermodynamic ordering is quite insignificant for the entire Earth's surface.

It should be noted that life is frequently dependent upon entropy reducing processes not produced by life itself. For example, most species of green plants need fresh water; and the entropy of fresh water is less than the entropy of salt water. sunlight evaporates pure water from the ocean and land. When this pure water condenses out, fresh water falls as rain. Sunlight, thus, reduces the entropy of water from salt water to fresh water without any living agency being involved.

To estimate the entropy decrease from salt water to fresh water it is only necessary to consider the entropy of mixing. Water is in general highly chemical reactive with solutes, so a full detailed account would be very complicated and out of place here. According to statistical mechanics the statistical weight of a particular macrostate of a system is given as the number of microstates or ways in which the macrostate can be formed (Sears, 1953). In particular, if there are Z molecules then there are Z! ways that these molecues can be ordered. If there are n types of molecules, Z_i of each kind, then the statistical weight becomes (Epstein, 1937)

$$W = \left(\sum_{i=1}^{n} Z_i\right)! \; . \tag{10}$$

For the present case there are only two types of molecules involved, water molecules Z_w and solute molecules (or ions) Z_s (differences between solute molecules is of no interest here.). The entropy is given as

$$S = k \, ln \, W + S_0, \tag{11}$$

where the constant S_0 is of no concern here and where k is Boltzmann's constant,

$$k = R/N_0 = 1.37 \times 10^{-16} \text{ erg/K}, \tag{12}$$

where R = 1.99 cal/mole°K is the ideal gas constant and $N_0 = 6.06 \times 10^{23}$ is Avogadro's number. Since Z_w and Z_s are large numbers, Stirling's approximation,

$$ln(x!) = x \, ln \, x - x, \tag{13}$$

may be used; and Eq. (11) yields

$$S = k(Z_w + Z_s)\left[ln(Z_w + Z_s) - 1\right] + S_0. \tag{14}$$

The entropy when water and salt are present separately is given by

$$S = k(Z_w \, ln \, Z_w - Z_w + Z_s \, ln \, Z_s - Z_s) + S_0. \tag{15}$$

Thus, the entropy change from an initial state where the water and solute molecules are separated to a final state in which they are in solution together is given by the *entropy of mixing*, Eq. (14) minus Eq. (15),

$$\Delta S = k\left[(Z_w + Z_s)\, ln(Z_w + Z_s) - Z_w \, ln \, Z_w - Z_s \, ln \, Z_s\right]. \tag{16}$$

Introducing the ratio of the number of moles of solute to the number of moles of water,

$$g = Z_s / Z_w, \tag{17}$$

the entropy of mixing may be written as

$$\Delta S = R(Z_w + Z_s)\left[ln(1 + g) - g(ln \, g)/(1 + g)\right], \tag{18}$$

where R is the ideal gas constant and where Z_w and Z_s are now to be expressed as the number of moles of water and solute. In general g is assumed to be small. When g = 0 for pure water $\Delta S = 0$; for g = 1/100 the entropy of the solution per mole of solution is 0.091 cal/mole°K; for $g = 1/10$ it is 0.609 cal/mole°K; and for $g = 1/2$ it is 1.386 cal/mole°K.

Much of the mass transport required by life, such as wind, water circulation, and diffusion are not produced by life itself. However, life does contribute with motility, by moving material using cilia and peristalsis, generating mass flow with temperature gradients, causing diffusion with salt concentration gradients, etc. (Wesley, 1974g). The ordering of the Earth's surface couples together intimately both living and nonliving processes; although living processes are probably the more important.

It may be noted that the increase in biomass over geologic time probably means a corresponding increase in the rate of deposition of permanent low entropy detritus as ores and minerals (Meyer, 1985).

5. Nonliving Processes Ordering the Earth's Surface

As the Earth was formed, infall energy created thermodynamic order. The core, mantle, crust, ocean, and atmosphere were separated out with different chemical compositions, densities, and temperatures representing a corresponding vast decrease in entropy. Since the Earth formed about 4.5×10^9 years ago the entropy reducing processes have been dominated by the action of sunlight as indicated by Eq. (6). Never the less, some fossil or residual infall energy still exists to create thermodynamic order on the Earth's surface (Wesley, 1974h).

If the mean internal temperature of the Earth is taken to be 500°C and the heat capacity of the Earth is taken to be that of basalt of 0.2 cal/gm, then there are 2.5×10^{37} ergs of thermal energy stored in the Earth left over from the original infall energy to create the Earth and from radioactivity. Unfortunately this vast store of energy can create only a very small amount of thermodynamic order, as the heat conductivity of the Earth is so low. The Earth's heat flows to the surface at the rate of about 3×10^{20} erg/sec, which may be compared with 9.4×10^{23} erg/sec provided by sunlight on the Earth (Wesley, 1974i), which is about 3000 times greater. In addition the temperature differences that can be utilitzed are generally quite small, the temperature gradient in the Earth's crust being only about 1°C for every 30 meters of depth. The entropy production due to the Earth's heat in the upper 5 km of the crust is about

$$dS/dt = (dQ/dt)(1/T_e - 1/T_c) = 4 \times 10^{17} \text{ erg/sec°K}, \tag{19}$$

where $T_e = 290\text{K}$ is the temperature of the Earth's surface and $T_c = 460\text{K}$ is the temperature at a depth of 5 km. This result (19) may be compared with the entropy production from sunlight of 3×10^{21} erg/sec°K.

The potential to create thermodynamic order from the Earth's heat is even very much less than indicated by Eq. (19), as vertical mass transport mechanisms in the Earth are virtually nonexistent. The only significant (on a local scale) thermodynamic ordering that can take place due to the Earth's heat occurs where vertical mass transport occurs. Thus, ordering is associated with sea-floor spreading, magmatic flow in pipes and volcanoes, hot springs, tectonic flow and displacement, and collisions between continental plates. (In the Earth's mantle convection occurs, so the mantle is probably becoming slowly thermodynamically more ordered by virtue of the Earth's heat.) These sites and activities are preferred by geologists to explain ordering processes on the Earth (Meyer, 1985); but these processes are insignificant for the Earth's surface as a whole in comparison to the action of sunlight, as indicated by Eq. (6) and the discussion above.

There are very large entropy reducing processes on the Earth's surface powered by sunlight, which have nothing to do with life. Generally these processes are not associated with the permanent deposition of ordered compounds. These entropy reducing processes are primarily reversible or cyclic. For example, when water condenses out of air to form rain, there is a reduction of entropy of 1.5 cal/gmK.

And when water freezes into ice there is an entropy reduction of 0.27 cal/gmK. These processes are balanced by the reverse processes of evaporation and melting so that generally no net irreversible odering occurs.

The action of fresh water from rain dissolving salts from the Earth's surface can lead to permanent ordering. The water with solutes can penetrate many meters into the Earth where, due to changes in pressure, temperature, salinity, and chemistry the solutes can become deposited out as low entropy minerals such as evaporites. Sizeable ore and mineral deposits may arise from such percolative processes. The initial entropy reduction is powered by sunlight to convert salt water to fresh water, as explained above. Huge salt deposits from evaporated sea water represent low entropy deposits, as the salt in solution has a higher entropy. These deposits were clearly formed without the action of life. Life living in concentrated salt solutions might have incresed the amount of sunlight absorbed, however.

6. Entropy Reduction Due to Change from Small-Scale to Large-Scale Order

Apart from a few examples, the previous discussion has primarily assumed that the entropy of the surface of the Earth has decreased over geologic time, because it follows from the fundamental law that the entropy decreases with time in all natural thermodynamic statistical systems open to deep space. It is of considerable interest, however, to see if the Earth's surface has, in fact, decreased in entropy over geologic time. Direct evidence for such a decrease further helps 1) to establish the general fundamental law for ordering processes in nature and 2) to establish the entropy reducing character of life and the consequent physical law of evolution that states that life evolves in a direction such as to increase the biomass of the biosphere.

The early Earth's surface consisted of basaltic type rocks as in the Earth's mantle, meteorites, or moon rocks. Such rocks consisted of mixtures and solid solutions of minerals such as pyronenes, olivines, and iron-spinels in small crystals, grains, or granules of perhaps of the order of a millimeter in size. The original Earth rocks when viewed on the submillimeter scale appeared to have elements partitioned into small low entropy mineral grains. But when viewed on a 10 cm scale such rocks appeared to be a homogeneous mixture of elements with no partitioning into mineral grains. The original Earth rocks possessed *small-scale order*.

In contrast present-day surface crustal rocks in the upper 5 km of the Earth's crust appear dramatically different. They consist of low entropy minerals, which are frequently simpler with fewer elements, in large crystals, grains, or granules. The same mineral can extend over centimeters, meters, or even kilometers. Thus, for example, limestone, which was not present in the original basaltic type rocks exists today as a more-or-less pure calcium carbonate in vast contiguous deposits. It can, therefore, be said that present-day crustal rocks possess *large-scale order*.

Rarer elements are today in general distributed in smaller deposits or volumes; but in no case are the volumes as small today as the volumes containing the same elements in the original basaltic type rocks. Granite, which is derived from melted crustal rocks does not appear like mantle rocks. The crystals of quartz, feldspars, micas, beryls, etc. in acidic granite are generally very much larger than the crystals in mantle basalt. Thus, even granite tends to preserve the large-scale order of present-day crustal rocks.

The change from small-scale order to large-scale order means that the Earth's surface, or upper crust, has undergone a vast reduction in entropy that can be estimated. The frequent change from complex minerals containing many different elements found in mantle rocks to simpler minerals containing fewer elements found in present-day crustal rocks also generally constitutes an entropy reduction, as discussed in the following Section.

The entropy reduction associated with the change from small-scale to large-scale order can be estimated using statistical mechanics. When Z molecules are separated into n grains, each containing Z_i molecules, the statistical weight for the system becomes

$$W = Z! \Big/ \prod_{i=1}^{n} Z_i! \; ; \tag{20}$$

since the number of ways molecules are arranged within each grain $Z_i!$ does not change the macrostate of interest. To simplify the mathematics the case of n grains of the same size may be considered, so Eq. (20) becomes

$$W = Z! \big/ [(Z/n)!]^n . \tag{21}$$

From the definition, Eq. (11), of entropy Eq. (21) yields

$$S = \ln Z! - n \ln (Z/n)! + S_0 . \tag{22}$$

Since Z and Z/n are large numbers, Stirling's formula (13) may be used; and Eq. (22) becomes

$$S = Z \ln n + S_0 . \tag{23}$$

The change in entropy from the initial state where Z molecules are divided among a large number of grains n_i to the final state where Z molecules are divided among a small number of grains n_f is given by

$$\Delta S = kZ \ln (n_f / n_i). \tag{24}$$

Since the number of grains involved is proportional to a fixed volume V_0 divided by the volume of an individual grain; and since the volume of an individual grain is proportional to the grain size y cubed;

$$n = V_0/y^3 \qquad \text{or} \qquad n_f/n_i = (y_i/y_f)^3 . \tag{25}$$

Substituting Eq. (25) into (24) yields

$$\Delta S = - 3kZ \ln (y_f/y_i). \tag{26}$$

If the present-day grain size of crustal rocks is estimated to be 10 times greater than the grain size in the original basaltic type rock, then the decrease in entropy per mole of rock is

$$\Delta S = - 3R \ln 10 = - 5.7 \times 10^8 \text{ erg/mole}^\circ\text{K}. \tag{27}$$

If, however, it is estimated that there has been a hundred-fold increase in the size of grains, which may be true, then the decrease in entropy per mole of rock is

$$\Delta S = - 3R \ln 100 = - 1.1 \times 10^9 \text{ erg/mole}^\circ\text{K}. \tag{28}$$

Assuming a mean molecular weight for crustal rock of 100 and assuming a mass of 6.8×10^{24} gm for the upper 5 km of the Earth's crust, the total entropy reduction of the Earth's surface due to a change from small-scale to large-scale order is estimated to be

$$\Delta S = - 3.9 \text{ to } - 7.8 \times 10^{31} \text{ erg/K}. \tag{29}$$

This result may be compared with the entropy production that makes it possible for such entropy reducing processes, such as the change from small-scale to large-scale order to occur. The entropy production necessary to form the Earth out of a cloud of gas and dust from Eq. (5) is 1.6×10^{37} erg/K. The entropy production due to irradiation of the Earth by sunlight since it was formed from Eq. (3) is given by 4.9×10^{38} erg/K. Thus, it is seen that the entropy production is large enough to account for the entropy decrease given by Eq. (29).

It may be seen that the entropy reduction given by Eq. (29) is about 100 times greater than the entropy reduction of carbon to produce the Earth's atmospheric oxygen as given by Eq. (9) of -4.6×10^{29} erg/K. This provides the important conclusion that the role of carbon in ordering the Earth's surface is primarily that of a catalyst.

The thermodynamic order of the Earth's surface has clearly increased with geologic time.

7. Entropy Reduction Due to Ore Formation

The low entropy of numerous large ore and mineral deposits indicate the entropy reduction of the Earth's surface over geologic times. Such mineral species separate out from an original more-or-less undifferentiated mixture of elements. Ores and minerals are frequently deposited hydrothermally or by the action of life from aqueous solutions where a variety of solutes are present. The following estimate of the entropy reduction involved, while based upon the case of aqueous solutions, is not limited to such solutions. The end results obtained are valid for magmatic separation, mechanical separation, solid diffusion, or any process whatsoever that might give rise to ores and minerals of low entropy.

The statistical weight W of a particular macrostate of an aqueous solution of n solutes of Z_i molecues each is given by

$$W = \left(\sum_{i=1}^{n} Z_i\right)! \ , \tag{30}$$

where the water molecules are ignored (in contrast to Eq. (10)) as not giving rise to different macrostates by virtue of their permutations. For the formation of a particular ore or mineral only one type of solute is of interest, say type 1. The solution may then be characterized as having Z_1 solute molecules of type 1 and Z_2 solute molecules that are not type 1. Thus, the statistical weight W from Eq. (30) becomes

$$W = (Z_1 + Z_2)! \ . \tag{31}$$

From the definition of entropy, Eq. (11), and Stirling's formula (13) for Z_1 and Z_2 large, the entropy of the system is then

$$S_i = k\left[(Z_1 + Z_2)\, ln\,(Z_1 + Z_2) - (Z_1 + Z_2)\right] + S_o. \tag{32}$$

If the solution is separated into a solution of solute type 1 alone and a solution of solute type 2 alone, the final entropy is

$$S_f = S_1 + S_2 = k(Z_1\, ln\, Z_1 - Z_1 + Z_2\, ln\, Z_2 - Z_2) + S_o. \tag{33}$$

The entropy reduction in going between these two macrostates is then

$$\Delta S = S_f - S_i = k\left\{ Z_1\, ln\left[Z_1/(Z_1 + Z_2)\right] + Z_2\, ln\left[Z_2/(Z_1 + Z_2)\right] \right\}. \tag{34}$$

For ore or mineral formation the solute molecules of interest are usually rare, so $Z_1 << Z_2$. In this case

$$ln\left[Z_2/(Z_1 + Z_2)\right] \approx - Z_1/Z_2. \tag{35}$$

The entropy reduction from Eqs. (34) and (35) is then given simply by

$$\Delta S = - kZ_1\left[ln\,(Z_2/Z_1) + 1\right]. \tag{36}$$

As a specific example the separation of a copper salt from sea water may be considered, where the ratio of the total number of ions of all types to the number of ions with copper is about $Z_2/Z_1 = 7 \times 10^4$. Using Eq. (36) the entropy reduction involved is then about

$$\Delta S = - 24 \text{ cal/mole}^{\circ}\text{K}. \tag{37}$$

A single large copper ore deposit containing 10^{13} gm of copper (10 million metric tons) represents an entropy reduction of about 10^{20} erg/K. The Earth contains many such low entropy ore and mineral deposits which were derived from the original high entropy basaltic type rocks. The net entropy reduction represented by all of these ore and mineral deposits may well exceed 10^{30} erg/K.

Since the average relative concentration of the elements in the Earth's crust is roughly similar to sea water, ores separated out directly from the solid crust represent about the same entropy reduction as those derived from sea water.

Another more significant example is provided by silica sand, SiO_2. Silicon dioxide did not occur as a free mineral in the original basic basaltic type Earth rocks. To estimate the entropy reduction to form the sand found on the Earth's surface today it is only necessary to calculate the entropy reduction to precipitate SiO_2 from sea water where the ratio of all ions to SiO_2 is about $Z_2/Z_1 = 8 \times 10^3$. From Eq. (3) the entropy reduction is then

$$\Delta S = - 20 \text{ cal/mole}^\circ\text{K}. \tag{38}$$

If the Earth's crust is about 60 percent sand and the mass of the Earth's crust to a depth of 5 km is taken to be 6.8×10^{24} gm, then the Earth's surface crust contains about 4.1×10^{24} gm of sand. From Eq. (38) this represents a net entropy decrease of the surface of the Earth of about

$$\Delta S = - 5.9 \times 10^{31} \text{ erg/K}. \tag{39}$$

This result (39) may be compared with the entropy reduction associated with the change from small-scale to large-scale order as estimated by Eq. (29), which is the same order of magnitude.

From the present considerations of the entropy decrease associated with the formation of ores and minerals it is clear that the Earth's surface has, in fact, decreased over geologic time.

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