AN EFFICIENT LIGHTNING ENERGY SOURCE ON THE EARLY EARTH

R. D. HILL

Chem. & Nuc. Eng. Dept., University of California, Santa Barbara, CA 93106, USA

(Received December 30, 1991)

Abstract. Miller and Urey suggested in 1959 that lightning and corona on the early Earth could have been the most favorable sources of prebiotic synthesis. In 1991 Chyba and Sagan reviewed the presently prevailing data on electrical discharges on Earth and they raised questions as to whether the electrical sources of prebiotic synthesis were as favorable as was claimed. The proposal of the present paper is that localized lightning sources associated with Archaean volcanoes could have possessed considerable advantages for prebiotic synthesis over the previously suggested global sources.

1. Introduction

The role of electric discharges in synthesizing amino acids was demonstrated by Miller (1953), and the feasibility of organic material synthesis on the primitive earth by lightning was advanced by Miller and Urey (1959). Much further analysis and experimental work has been conducted since that time.

The problem of the efficiency of the lightning sources for organic synthesis in the early earth has recently been challenged by Chyba and Sagan (1991). They raised questions about whether the lightning and associated corona sources could have been as intense as proposed by Miller and Urey, and by subsequent workers as: Miller and Orgel (1974) and Miller, Urey and Oró (1976). Chyba and Sagan concluded that the amounts of energy dissipated by terrestrial lightning and corona could have been factors of 20 and 120, respectively, less than the values estimated by Miller and Urey.

A second problem with regard to lightning synthesis process is the question of the character of the atmosphere existing on the earth at the time of prebiotic evolution. As noted by Stribling and Miller (1987), there has been considerable controversy – as given in the papers by Chang *et al.* (1983), Holland (1984), Lewis and Prinn (1984), Levine (1985), Walker (1987) – concerning the composition of the primitive earth's atmosphere. In the original Miller and Urey proposal it was assumed that the earth's early atmosphere was strongly reducing. In the original Miller experiment, a mixture of ammonia, methane and hydrogen was added to a flask containing water at room temperature. In the later experiment of Schlesinger and Miller (1983), the production efficiencies of hydrogen cyanide and formaldehyde were measured in a number of gas mixtures containing CO, CO_2, N_2, H_2O and H_2, that provided H_2/CO and H_2/CO_2 ratios of order of, and larger than, unity.

The purpose of the present paper is to suggest that the lightning associated with

Origins of Life and Evolution of the Biosphere **22**: 277–285, 1992.

early earth volcanoes could have been a much more effective source of the prebiotic synthesis process than the general earth lightning that has been inherently assumed by Miller and coworkers and by Chyba and Sagan in their review. [As noted by Miller and Orgel (1974), 'the value (of the available lighting energy) in the primitive earth is unknown' ... and ... 'there are several mechanisms for charge generation in thunderstorms and the relative importance of these could be greatly altered in a reducing atmosphere...'] We propose that the high efficiency of volcanic lightning could have been associated with the highly localized character of lightning over a water containment area that was both shallow and area-limited and could therefore have led to more highly concentrated solutions of synthesized organic molecules. The second factor that could have been responsible for a higher efficient production by volcanic lightning was the fact that the electric discharges actually occurred in the reducing gases of the volcanic plume itself. The following discussion attempts to establish these enhanced efficiencies.

2. Volcanic Lightning

There is a considerable literature on lightning activity associated with volcanoes; however, we draw mainly on the information gathered by the Office of Naval Research and Icelandic Groups, Anderson *et al.*, 1965 at the Surtsey Island volcano commencing on Nov. 14, 1963. In this event, the eruption occurred initially at a depth of 150 m below the sea surface, and in ten days had built up an island to a height of 100 m above sea level. Most of the lightning observed at Surtsey was associated with the clouds of tephra and steam from inside the volcanic cone, into which the sea water flowed. Later in the Surtsey Island development, however, significant lightning and charge generation in the steam cloud was observed to occur when molten lava flowed from the cone into the surrounding sea. An intense positive charge flow was generated in the upward rising tephra and steam cloud above the cone. Lightning occurred from the positively charged effluents either to negatively charged pockets of gas electrostatically induced by the positive effluents or to the volcanic island. The frequency of the externally visible Surtsey lightning strikes was as high as 10 min^{-1}, but the average rate was probably only about 30 flashes hr^{-1}. The activity of the Surtsey volcano continued for approximately one year, but there were many periods when the eruption frequency was significantly diminished.

According to Vonnegut (1963), the energy dissipated by a typical lightning flash in the Surtsey volcano was of the order of 10^6 J. Considerable effort was made by the ONR and Icelandic researchers to locate the lightning origins. In all cases, these were found to be within either the tephra or the immediately generated steam cloud above the volcanic cone. For most of the lightning observed, the tops of the visible discharges were at only about 200 to 300 m above the sea level and the top of the cloud above the lightning was only about 500 to 700 m above the ocean. In the Surtsey Island eruptions it was found that heavy, negatively charged, rain fell together with the tephra projected from the volcano, and most of the tephra fell within a distance of order 2 km from the cone. Although very small size tephra was still observed within distances of the order of 100 km, most of the precipitable ejecta appeared to be deposited, together with the rain, within a distance of order 10 km.

As seen in the time-lapse motion pictures taken at Surtsey, there is no doubt that practically all of the lightning flashes took place within the volcanic plumes. Thus, as far as the atmospheric chemistry is concerned, most of the electric discharge prebiotic synthesis must have occurred in the immediate volcanic plume gases and not in the general atmosphere of the Archaean age. As far as the primary Archaean volcanic gases were concerned, Holland (1984) concluded that 'the early volcanic gases released at low atmospheric pressures in equilibrium with metallic iron would have consisted largely of H_2 and H_2O, CO would have been the dominant carbon species, and H_2S would have contained the dominant sulphur species.'

3. Organic Synthesis by Volcanic Lightning

The question of whether volcanoes themselves could have been the source of organic synthesis was discussed by Miller and Orgel (1974). However, Miller and Orgel addressed their enquiry only towards the thermal energy of volcanoes. They estimated that only 0.13 calories per cm^2 yr^{-1} would be released from 1 km^3 yr^{-1} of volcanic lava and that this would be more than an order of magnitude less than the required release for effective organic synthesis in the Archaean era. In the present proposal, it is put forward that the Archaean volcanoes which were located in shallow depth water pools were the sources of intense lightning and that these electrical discharges were in fact capable of raising the concentrations of organic synthesized molecules above those already calculated to have been produced by the earth's general surface lightning.

In order to appreciate the modifications brought about by volcanic lightning we will first estimate the effect of localization of the lightning source and then, in the next section, attempt to evaluate the effect of the volcanic plume gases on the organic molecule production efficiency. In the present section, estimates of the production of HCN will follow the procedure already used by Miller and Orgel. These calculations are presented in Table I. Specific values used in this table are discussed under the following items.

SINGLE FLASH ENERGY

Miller and Orgel (1974) gave values of 0.9 calories per cm^2 yr^{-1} for ordinary lightning and 3 calories cm^{-2} yr^{-1} for corona accompanying storms. These values are together (see line 6 of Table I) the equivalent of a total energy of 16 J cm^{-2} yr^{-1}. For 100 flashes per second and for an earth's lightning area of 5.1×10^{18} cm^2 the energy per lightning flash is therefore produced by an average single flash energy of 6.0×10^9 J/flash, as shown in Table I. In the case of the Chyba-Sagan (1991) analysis, the lightning flash and corona discharge energies are approximately 1/20th

TABLE I

HCN concentrations produced by electrical discharges

Quantity	Lightning (Miller-Orgel)	Corona (Miller-Orgel)	Lightning (Chyba-Sagan)	Corona (Chyba-Sagan)	Lightning (Volcanic)
Single Flash Energy (J)	6.0×10^9	-	3.2×10^8	-	10^6
Lightning Area (cm^2)	5.1×10^{18}	5.1×10^{18}	5.1×10^{18}	5.1×10^{18}	10^{10}
Water Catchment (cm^2)	3.6×10^{17}	3.6×10^{17}	3.6×10^{17}	3.6×10^{17}	10^{11}
Flash Frequency (sec^{-1})	100	-	100	-	10^{-2}
Energy per yr ($J\ yr^{-1}$)	1.9×10^{19}	6.3×10^{19}	1.0×10^{18}	5.0×10^{17}	3.2×10^{11}
Energy source ($J\ cm^{-2}\ yr^{-1}$)	3.7	12.4	0.2	0.1	3.15
Energy/HCN mole ($J\ mole^{-1}$)	9.1×10^8	9.1×10^9	9.1×10^8	9.0×10^9	9.0×10^6
HCN Production (mole $cm^{-2}\ yr^{-1}$	4.1×10^{-9}	1.4×10^{-9}	2.2×10^{-10}	1.1×10^{-11}	3.5×10^{-7}
Catchment Volume (L)	1.4×10^{21}	1.4×10^{21}	1.4×10^{21}	1.4×10^{21}	5.0×10^{11}
Volume/Area ($L\ cm^{-2}$)	2.7×10^2	2.7×10^2	2.7×10^2	2.7×10^2	5.0
HCN Concentration (mole $L^{-1}\ yr^{-1}$)	1.5×10^{-11}	5.0×10^{-12}	8.2×10^{-13}	4.1×10^{-14}	7.0×10^{-8}

and 1/120th, respectively, of the Miller-Orgel values. The flash energy of 10^6 J/flash in the case of a volcanic lightning flash is taken from Vonnegut (1963). It is noted that this energy value is probably a minimum, especially since it does not include any contribution from corona, which in Miller and Orgel's case was more than three times larger than the direct lightning stroke energy.

LIGHTNING AREA

In the case of earth-wide lightning this value is taken as the earth's area. However, it is known that at present the lightning flashes are not evenly distributed over land and sea areas equally. In the case of volcanic lightning, a single volcanic area is taken from Surtsey's time lapse photography on the night of February 4, 1964 to be of the order of 1 km^2.

WATER CATCHMENT AREA

In the earth-wide lightning case, this area is assumed to be that of the present day oceans. In the case of a localized volcanic center, the water catchment area is taken to be approximately 10 km^2, which is that of a small pool assumed to be surrounding the volcano. From the Surtsey time lapse photographs it is seen that most of the intense fall out of tephra and heavy rain occurred within about 3 km of the cone, i.e. within an area of about 10 km^2. There is little doubt that this area is a minimum estimate. However, comments concerning the characteristics of the Archaean oceans are well known, e.g. 'the Archaean oceans were obviously present, but were they simply puddles?' (See Nisbet, 1987; Towe, 1983). The estimate of a small catchment area clearly enhances the ultimate concentrations of organic synthesized molecules; however, it will later be argued that the ratio of the volume of the catchment water compared to its catchment area is the more important factor in determining concentrations. Most of the lightning occurs at low altitudes, and it is suggested that the bulk of the HCN produced could have been quickly rained out to the pool. However, as critically discussed by Cicerone and Zellner (1983), the published information on the solubility of HCN in rainwater is conflicting. They concluded that HCN is not very soluble in water at 18 °C and at low partial pressures less than 1 torr. In a volcanic plume, the question of HCN's precipitation by either rain, steam, or adsorption by tephra particles or by salt aerosols, is clearly a complicated question. As pointed out by one of the reviewers, aqueous HCN is rather volatile and therefore could rapidly evaporate from solution. Clearly this point and other HCN catchment questions need still to be addressed.

Flash frequency

As far as general earth lightning is concerned, this rate is taken to be 100 flashes sec^{-1}. This point was discussed closely by Chyba and Sagan, and its value appears to be a reasonable one for present day lightning. In the case of volcanic lightning, the flash frequency is taken to be only 10^{-2} flashes sec^{-1}, or approximately one flash every two minutes. This value is much less than the most intense rate observed on Surtsey, or approximately one flash every six seconds. However, the necessary frequency is that averaged over the lifetime of a volcano. This duration which as far as the values in the table here apply is one year. The possibility of a considerable number of individual volcanic cones within the same Archaean pool area has also been noted by geologists.

Flashes per year

Here the year is taken to be the same as at present, or 3.15×10^7 sec. The values of the flashes per year are: $3.15 \times 10^9\ \text{yr}^{-1}$ in earth-wide lightning; and $3.15 \times 10^5\ \text{yr}^{-1}$ in volcanic lightning.

Energy source

These values for Miller-Orgel are the same as 0.9 and 3.0 calories/cm^2 yr. For Chyba-Sagan, the values are approximately 1/20th and 1/120th of the Miller-Orgel values. In the case of volcanic lightning, the value of $3.2\ \text{J cm}^{-2}\ \text{yr}^{-1}$ is the energy of $3.2 \times 10^{11}\ \text{J yr}^{-1}$ divided by the water catchment area.

Energy per mole of HCN

Because of its dependence on the nature of the electrical discharge and on the characteristics of the atmospheric medium in which the discharge occurs, choice of an energy value per mole of HCN can be difficult. As Miller and Orgel originally stated: 'some sample calculations' were based on a value of the HCN production efficiency equal to 100 k cal per HCN mole. Following later experiments by Schlesinger and Miller (1983), and by Stribling and Miller (1987), as well as by many other workers, this efficiency – as recently shown in the review by Chyba and Sagan (1992) – has since been considerably reduced from the Miller-Orgel value. The problem of choosing a particular HCN efficiency will be discussed later in Section 4, but the values shown in line 7 of Table 1 were chosen on the basis of the following assumed relevant conditions.

Miller-Orgel lightning: neutral atmosphere: 9.1×10^8 J mole^{-1}
Miller-Orgel corona: neutral atmosphere 9.1×10^9 J mole^{-1}
Chyba-Sagan lightning: neutral atmosphere: 9.1×10^8 J mole^{-1}
Chyba-Sagan corona: neutral atmosphere: 9.1×10^9 J mole^{-1}
Volcanic lightning: reducing atmosphere: 9.0×10^6 J mole^{-1}.

The efficiencies shown were chosen mainly from Chyba and Sagan's (1992) Table 2. In particular we note that Chyba and Sagan stated that in CH_4 atmospheres they scaled down efficiencies relative to the reducing case by a factor of 10^2.

HCN PRODUCTION

The total Miller-Orgel production, obtained by adding together the productions by lightning and corona, is seen equal to 5.43×10^{-9} moles cm^{-2} yr^{-1}. A value of 3.5×10^{-7} moles cm^{-2} yr^{-1} for the production by a lightning volcano is estimated. Chyba and Sagan's amended values of the energy in general lightning and corona yield only a production of 2.3×10^{-10} moles cm^{-2} yr^{-1}.

OCEAN VOLUME

Miller and Orgel (1974) assumed that the value of this factor was the present volume of the earth's oceans, i.e. 1.37×10^{21} L according to Sverdrup (1954). Stribling and Miller (1987) also used approximately this same value. For the volcanic case, the volume of the effective water pool surrounding the volcano is assumed to be only 5×10^{11} L which corresponds to a water catchment area of 10^{11} cm^2 and a water depth of 50 m. The question of the volume of the catchment water medium is discussed further in the next item.

HCN CONCENTRATIONS

As seen by the final row of entries in Table I, the estimated concentration of the HCN production rate in the volcanic lightning case is approximately 5 000 times larger than the concentration produced by Miller and Orgel's general lightning rate, and approximately 85 000 times larger than the amended production rate estimated by Chyba and Sagan.

The most important factor in the conversion from mole production per unit area yr^{-1} to mole concentration per unit volume yr^{-1} is the depth of the catchment volume. In the case of the volcanic lightning catchment pool, the depth, as seen from the volume to area ratio used, has been taken as 50 m. This choice was motivated by the information emerging from developments in Archaean geology. McCall (1981) claimed that 'there were numerous greenstone depositories ... that were not very deep.' Hickman (1981) claimed in the Australian Pilbara Block that 'local deformation was followed by the development of calc-alkaline volcanic centers in a generally shallow water environment.' Dunlop and Buick (1981) proposed that the geological formations in the Warrawoona Group (3.59 Ga – 3.3 Ga) of the

Pilbara Block indicated 'the existence of large shallow basins studded with calc-alkaline volcanoes and locally with evaporitic lakes.' Barley (1981), who carried out much of the basic research on the Pilbara Block, claimed that 'widespread massive and pillowed flows containing between 20 and 40% vesicles indicate that lavas were commonly erupted into shallow water (i.e. less than 200 m.).' The fact that 'a single flow of 50 m can be traced for more than 5 km,' and also the fact that 'lateral continuity of the thin (less than 5 m thickness) cherty sedimentary horizons for over 10 km' indicates an 'environment with a subdued topography.' Based mainly on these data, an average thickness of the catchment pool from center to the edge was assumed 50 m.

The nature of a water catchment volume associated with Archaean volcanoes is clearly an important question relative to the issue of prebiotic organic synthesis by lightning. Since the early Earth sea, however, is attributed to emission of water vapor from the earliest volcanoes, it is clear that at least in the earliest stages the volume of the sea surrounding volcanoes must have been small. Furthermore, fluctuations in the area distributions of volcanoes on the early Earth's surface must have been associated with inhomogeneities in the earliest crust or with the mechanics of instabilities causing extrusions of lava through the crust. These problems may possibly be addressed in the future by modeling.

4. Effect of Atmospheric Environment on HCN Production

An attempt is made in this section to address the problem that volcanic lightning and general earth lightning are expected to have occurred in different gaseous environments.

The whole field of organic synthesis on the early Earth has recently been reviewed by Chyba and Sagan (1992). In the case of lightning they made assessments of the production efficiencies of HCN synthesis in various atmospheres. They distinguished the 'reducing atmosphere' and the 'neutral atmosphere,' and following mainly the work of Schlesinger and Miller (1983) and of Stribling and Miller (1987), defined a partly reducing atmosphere as one given by an H_2/CO_2 ratio of order of 'several,' and a neutral atmosphere as one given by an H_2/CO_2 ratio equal to 0.1. In Table 2 of Chyba and Sagan's review, the following production efficiencies were given for lightning and coronal discharges, respectively: 3×10^{-9} and 3×10^{-10} kg J^{-1} in a reducing atmosphere, and 3×10^{-11} and 3×10^{-12} kg J^{-1} in a neutral atmosphere. [It is to be noted that these efficiencies are much lower than the value used by Miller and Orgel in their sample calculation. Thus the value of 3×10^{-11} kg J^{-1} (lightning-neutral) may be compared with Miller and Orgel's value for HCN of $1/4.2 \times 10^5$ J mole^{-1}, or 6.5×10^{-8} kg J^{-1}, i.e. approximately 2000 times larger in the cases of lightning in a neutral atmosphere.] According to Chyba and Sagan's Table 2, the amended HCN productions by lightning and corona, respectively, are: 3×10^7 kg yr^{-1} and 2×10^6 kg yr^{-1} for a neutral atmosphere.

An attempt is now made to estimate the HCN production efficiency for lightning occurring entirely in the gases emerging from the plume of an Archaean volcano. First, let us recall that Chyba and Sagan (1992) in evaluating the non-reducing effect of an Archaean atmosphere, placed reliance on Walker's (1977) conclusion that the 'partial pressure of CO_2 in the terrestrial atmosphere very early in earth history ... could have been as large as 10 bar'. For such a high output of CO_2 it would appear that the H_2/CO_2 ratio in the early atmosphere would have had values less than unity and therefore that the HCN production efficiencies would have been relatively low. In as far as volcanic lightning is concerned, however, we suggest two main reasons for assuming that the conditions in the gaseous volcanic plumes could have been very much different from those used by Chyba and Sagan for the external Archaean atmosphere. The first reason is that Walker's conditions pertained largely 'during the course of earth accretion – or very shortly thereafter,' i.e. according to Chyba and Sagan 'sometime before 3.8 Ga ago.' It does not seem beyond the bound of possibility that the prebiotic period of main interest was somewhat less than 3.8 Ga. The second reason is that Holland (1984) identified the dominant gaseous species in the Archaean volcanic plume as having the following abundances: $H_2/H_2O \approx 2.3$, $CO/CO_2 \approx 6$, $CH_4 << CO_2$. We will assume that a possible value for the H_2O/CO_2 ratio in Archaean times was similar to the ratio existing in present times. From Heald *et al.*'s (1963) data of gases issuing from gas-filled cracks from the cinder cone of the Kilauea Iki volcanic crater, we estimate, that H_2O was 40 times more abundant than CO_2, and therefore it is estimated that in Archaean times the H_2/CO_2 ratio could have been of the order of 100 to 1. If this were the case, then the gases issuing from Archaean plumes could have satisfied the criterion for a highly reducing atmosphere with H_2/CO_2 much larger than unity. It is not known from experiment how the efficiency of HCN production in such a highly reducing atmosphere, especially in the presence of such a high concentration of water vapor, might be increased above the values used by Chyba and Sagan for the general atmosphere. It is suggested, however, that the production efficiency might have approached, or may have been even larger than, the value of 9×10^6 J mole^{-1}, which is Chyba and Sagan's value for lightning in a reducing atmosphere.

5. Concluding Remarks

Finally, it must be said that it seems remarkable that the volcanic lightning source of prebiotic synthesis has not already been suggested in the scientific literature. The only reference known to the present author has been at the end of Blanchard's (1967) book *From Raindrops to Volcanoes*, when he stated that 'many other scientists have visited Surtsey, their interests have ranged from chemical changes in the sea to biological studies on the new volcanic soil.' This is not quite the question that has been raised in this paper. Perhaps other questions were raised but they may have escaped the publication field.

Acknowledgement

Dr Christopher Chyba's helpful comments on the manuscript during its review and on the possible applicability of his 1992 article with Dr Sagan to the manuscript topic are deeply appreciated. Further helpful comments on the manuscript by an anonymous reviewer are also acknowledged.

References

Anderson, R., Björnsson, S., Blanchard, D. C., Gathman, S., Hughes, J., Jónasson, S., Moore, C. B., Survilas, H. J., and Vonnegut, B.: 1965 *Science* **148**, 1179.

Barley, M. E.: 1981, *Archaean Geology*, J. E. Glover and D. I. Groves (eds.), Geol. Soc. Aust. Inc., Sydney, p. 263.

Blanchard, D. C.: 1967, *From Raindrops to Volcanoes*, Doubleday & Co., Garden City, New York.

Chang, S., Des Marais, D., Mack, R., Miller, S. L., and Strathearn, G. E.: 1983, *Prebiotic Organic Synthesis and the Origins of Life*, Ch 4, in *Earth's Earliest Biosphere: Its Origin and Evolution*, J. W. Schopf (ed.), Princeton Univ. Press, Princeton, New Jersey.

Chyba, C. and Sagan, C.: 1991, *Origins of Life* **21**, 3.

Chyba, C. and Sagan, C.: 1992, *Nature* **355**, 125.

Cicerone, R. J. and Zellner, R.: 1983, *J. Geophys. Res.* **88**, 10689.

Dunlop, J. S. R. and Buick, R.: 1981, *Archaean Geology*, J. E. Glover and D. I. Groves (eds.), Geol. Soc. Aust. Inc., Sydney, p. 225.

Heald, E. F., Naughton, J. J., and Barnes, I. L.: 1963, *J. Geophys. Res.* **68**, 545.

Hickman, A. H.: 1981, *Archaean Geology*, J. E. Glover and D. I. Groves (eds.), Geol. Soc. Aust. Inc., Sydney, p. 57.

Holland, H. D.: 1984, *The Chemical Evolution of the Atmosphere and Oceans*, Princeton Univ. Press, Princeton, New Jersey. (See also Chang *et al.*, 1983, Secs. 4-2-4).

Lewis, J. S. and Prinn, R. G.: 1984, *Planets and Their Atmospheres*, Academic Press, Orlando, Florida.

Levine, J. S.: 1985, *The Photochemistry of Atmospheres*, Academic Press, Orlando, Florida.

McCall, G. J. H.: 1981, *Archaean Geology*, J. E. Glover and D. I. Groves (eds.), Geol. Soc. Aust. Inc., Sydney, p. 3.

Miller, S. L.: 1953, *Science* **117**, 528.

Miller, S. L. and Urey, H. C.: 1959, *Science* **130**, 245.

Miller, S. L. and Orgel, L. E.: 1974, *The Origins of Life on the Earth*, Prentice-Hall, Edgewood Cliffs, New Jersey.

Miller, S. L., Urey, H. C., and Oró, J.: 1976, *J. Mol. Evol.* **9**, 59.

Nisbet, E. G.: 1987, *The Young Earth*, Allen and Unwin, Boston, Massachusetts.

Schlesinger, G. and Miller, S. L.: 1983, *J. Mol. Evol.* **19**, 383.

Stribling, R. and Miller, S. L.: 1987, *Origins of Life* **17**, 261.

Sverdrup, H. U.: 1954, *The Earth as a Planet: The Solar System*, Vol. II. G. P. Kuiper (ed.), University of Chicago Press, Chicago, Illinois.

Towe, K. M.: 1983, *Precambrian Research* **20**, 161.

Vonnegut, B.: 1963, *Meteorol. Monographs* **5**, 231.

Walker, J. C. G.: 1985, *Origins of Life* **16**, 117.

Walker, J. C. G.: 1987, *Evolution of the Atmosphere*, Macmillan, New York, New York.