considerations suggest that doses in the range of 500 r could have severely decimated many animal populations directly or indirectly, whereas the affected plants could have ultimately survived through their radioresistant seeds and spores. Furthermore, if the biologic community were seriously disrupted it could allow the proliferation and radiation of animal and plant species that were able to take advantage of the change in the environment. The pattern of biologic evolution following radiation has recently been discussed in detail by Woodwell (*21*).

It was Schindewolf's position that high-energy radiaton might penetrate to depths sufficient to cause the extinction of marine organisms, either directly or by means of secondary effects, such as the formation of radioactive isotopes. More recently, Loeblich and Tappan (*4*) have suggested that the mass extinction of planktonic organisms at the close of the Permian period might conform to a pattern expected of cosmic radiation. The intensity of the ionizing component of cosmic radiation in water varies with depth according to

$$J_x = J_0 (1 + 0.1x)^{-2.1} \qquad (4)$$

where x is the depth in meters. A dose of 1000 r would yield only 72 r after penetrating 25 m of water. A dose of 5000 r would be reduced to 116 r after penetrating 50 m. Thus, most planktonic life (both plant and animal) would be protected since they occur at greater depths. Also, fish and other marine animals found at depths greater than 25 to 50 m would be protected against doses as great as 5000 r. However, it is obvious that those marine organisms living in shallow water would be vulnerable. In particular this group might include amphibians and some marine reptiles.

As for the secondary effect of the radioactive decay of isotopes produced by cosmic rays, our estimates show that such effects are of little significance if one assumes doses in the range estimated.

The above considerations suggest that cosmic radiation from exploding supernovae could have caused the extinction of many exposed animals, including some marine organisms, without the simultaneous extinction of plant life. This is an attractive finding since it conforms to one of the most puzzling aspects of mass extinction. It is also interesting that mass extinctions have occurred approximately once every 60 million years since Cambrian times. Our estimates show that a dose of at least 50 r should occur once every 50 million years. However, radiation from supernova explosions cannot account for the extinction of small marine organisms (protozoans and algae), at least for the doses estimated in this study.

While it is true that the parameters involved in making these calculations are poorly known, it is perhaps more than coincidental that the estimates of these parameters should lead to calculated doses that are roughly necessary to produce some of the patterns of mass extinction observed in the geologic record.

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Ammonium Ion Concentration in the Primitive Ocean

Abstract. *If ion exchange on clay minerals regulated the cations in the primitive ocean as it does in the present ocean, the* pH *would have been 8 and the* K^+ *concentration 0.01*M. *Since* NH_4^+ *and* K^+ *are similar in their clay-mineral equilibria, the maximum* NH_4^+ *concentration in the primitive ocean would also have been 0.01*M. *An estimate of the minimum* NH_4^+ *concentration is* 1×10^{-3}M, *based on the reversible deamination of aspartic acid and the assumption that aspartic acid is necessary for the origin of life. The rate of this nonenzymic deamination is rapid on the geological time scale.*

Although the presence of NH_3 is considered important in the synthesis of organic compounds on the primitive Earth (*1*), there have been no quantitative estimates of the concentrations based on the organic chemistry or on detailed atmospheric models (*2*). The stable species of nitrogen would have been ammonia under the generally accepted reducing conditions, but most of this NH_3 would have dissolved in the ocean to form a mixture of NH_4^+ and NH_3, the ratio depending on the *p*H. The available nitrogen places one upper limit on the NH_4^+ concentration. If all the nitrogen in the atmosphere (755 g/cm²) were placed in the present ocean (282 liter/cm²) as NH_4^+, the concentration would be 0.19*M*. If the primitive ocean were smaller or the nitrogen in the rocks is included, the concentration would be correspondingly higher.

This upper limit would be reduced by the clay minerals. The *p*H and the cations in the present ocean are regulated largely by the clay minerals, as was first suggested by Sillén (*3*) and discussed by others (*4, 5*). This regulation is based on the fact that the ion-exchange capacity of the oceanic sediments is large compared to the H^+ and the buffer capacity of the ocean. The ion-exchange capacity also appears to be sufficient to regulate the concentrations of Na^+, K^+, Ca^{++}, and Mg^{++}. The ion-exchange equilibrium between H^+ and K^+, as well as the other cations, controls the *p*H of the oceans at 8.1.

We can expect that a similar regulation of cations took place in the primitive ocean as long as there was a sufficient amount of weathering and sedimentation. These considerations suggest that the *p*H of the primitive ocean also was about 8. At this *p*H the ammonia in the ocean would have been mainly NH_4^+, and NH_4^+ would have entered into the clay-mineral ion-exchange equilibria.

The exchange of NH_4^+ and K^+ on the clay minerals

$$NH_4^+ + \text{clay} \cdot K^+ = K^+ + \text{clay} \cdot NH_4^+$$

should have an equilibrium constant of about 1.0 since NH_4^+ and K^+ are very similar in clay-mineral and other silicate-mineral reactions (*6*). In particular, the equilibrium constant for this reaction on montmorillonite (*7*) is 1.40, while a similar equilibrium for Na^+ and K^+ is 0.25. These equilibrium constants are for 25°C, but they are almost independent of temperature ($\Delta H = 1$ to 3 kcal). The exchange with montmorillonite should be representative of most layered silicates.

The dynamic process for the regulation of potassium in the ocean involves uptake of the excess potassium entering from rivers (*5*). The molar ratio of sodium to potassium entering the ocean from rivers averages 4.6, but the ratio in seawater is 46. Most of this excess potassium from rivers is removed in formation of the framework of potassium-rich minerals, with the final adjustments of the potassium concentration taking place on the exchangeable sites of the clay. Although all the minerals involved in this process are not known, the net result of this ion exchange leads to a K^+ concentration in the present ocean of 0.01*M*. A similar regulation of NH_4^+ would be expected on the primitive Earth unless the cations, alumina, and silica entering the oceans from the rivers were very different. If the NH_4^+ in the rivers was in greater concentration than the K^+, the NH_4^+ would have been taken up preferentially by the clay minerals. This uptake would continue, if the sediments were in excess, until the NH_4^+ and K^+ were approximately equal in concentration and close to the present 0.01*M* K^+. This excess NH_4^+ in the rivers could have come from the weathering of rocks containing NH_4^+, or from the NH_3 in the atmosphere.

If the NH_4^+ in the rivers was in lower concentration than the K^+, the NH_4^+ in the oceans also would have been lower than the K^+, with a corresponding decrease in the NH_4^+ content of the clay minerals. This is the situation today, where the concentration of NH_4^+ in the rivers is very low and variable. Therefore this ion-exchange process on the clay minerals establishes an upper limit on the concentration of NH_4^+ in the ocean, but it does not regulate NH_4^+ at low concentrations.

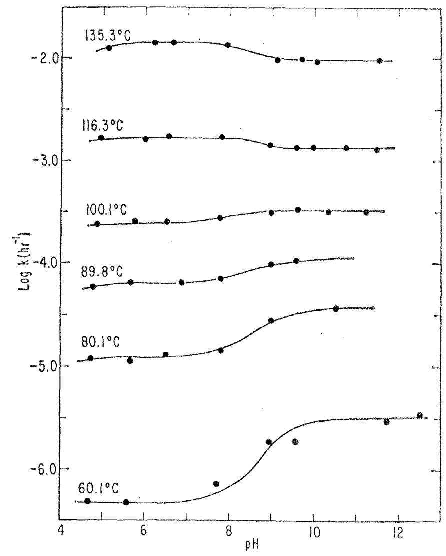
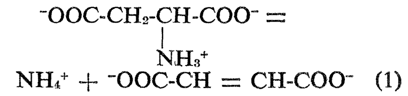


Fig. 1. Rate of deamination of aspartic acid as a function of *p*H and temperature.

An estimate of the lower limit of the NH_4^+ concentration can be obtained from the prebiological organic chemistry since a number of these syntheses require NH_3. The kinetics and equilibria can fix the optimum concentrations for efficient synthesis of the compounds presumably needed for life to arise. A relevant equilibrium of this type is the decomposition of aspartic acid to ammonia and fumaric acid:



$$^-OOC\text{-}CH_2\text{-}\underset{\displaystyle NH_3^+}{\underset{|}{CH}}\text{-}COO^- = NH_4^+ + {}^-OOC\text{-}CH = CH\text{-}COO^- \quad (1)$$

In decomposition aspartic acid differs from most amino acids. Abelson and Vallentyne (*8*) have shown that alanine, serine, phenylalanine, and glutamic acid decompose by a slow ($t_{\frac{1}{2}} = 10^{11}$ years at 25°C for alanine) irreversible decarboxylation.

Aspartic acid decomposes by a deamination, which is reversible and rapid on the geological time scale. Of the amino acids that occur in proteins, only aspartic acid and asparagine are known to undergo this type of chemical decomposition, although there are enzymes that can deaminate histidine, phenylalanine, and tyrosine (*9*).

The equilibrium constant for Eq. 1

$$(NH_4^+) = K[(\text{DL-aspartate})/(\text{fumarate})]$$

has been measured enzymically (*10*, *11*) and nonenzymically (*10*) between 5° and 135°C and is given by the equation

$$\log K = +8.22 - 2276/T - 0.0106T$$

The equilibrium constant is essentially independent of *p*H between 5 and 9; the aspartic acid is less stable outside this *p*H range. Malic acid can be formed from the fumaric acid (*12*), but we shall omit this complication.

The likely syntheses of aspartic acid on the primitive Earth are from a Strecker synthesis with $NC\text{-}CH_2CHO$ or its equivalent (*13*), from cyanoacetylene (*14*), from ammonium cyanide (*15*), or from hydrogen cyanide alone (*16*). Although the last synthesis does not require ammonia, any aspartic acid made by this process would have decomposed until the equilibrium of Eq. 1 was reached. If there was no NH_4^+ in the primitive ocean, the aspartic acid would have entirely decomposed to fumarate.

The heterotrophic hypothesis of the origin of life assumes that the basic constituents of the first living organism were available in large quantities in the primitive ocean; we shall assume that aspartic acid was one of these constituents. Although the concentration of aspartic acid in the primitive ocean cannot be estimated, we shall assume

Table 1. Equilibrium concentrations of ammonia and hydrogen.

Item	Temperature (°C)		
	0	25	50
	Upper limit from clay mineral equilibrium		
NH_4^+ (*M*)	0.01	0.01	0.01
NH_3 (*M*)	6.0×10^{-5}	4.2×10^{-4}	2.1×10^{-3}
pNH_3 (atm)	2.9×10^{-7}	7.3×10^{-6}	1.0×10^{-4}
pH_2 (atm)	1.6×10^{-7}	4.3×10^{-6}	6.3×10^{-5}
	Lower limit from aspartic acid equilibrium		
NH_4^+ (*M*)	1.0×10^{-3}	2.7×10^{-3}	5.8×10^{-3}
NH_3 (*M*)	6.0×10^{-6}	1.1×10^{-4}	1.2×10^{-3}
pNH_3 (atm)	2.9×10^{-8}	1.9×10^{-6}	5.9×10^{-5}
pH_2 (atm)	3.5×10^{-8}	1.8×10^{-6}	4.5×10^{-5}

that the ratio of aspartic to fumaric acid did not fall substantially below 1.0. This criterion may be too restrictive, and it is possible that life could have arisen if much less aspartic acid had been present on the primitive Earth. On the basis of these assumptions we can say that the minimum concentration of NH_4^+ in the primitive ocean would be given by the K from Eq. 1, $1.0 \times 10^{-3}M$ at 0°C and $2.7 \times 10^{-3}M$ at 25°C.

It remains to be shown that this equilibrium would have been attained in the time available, which was less than 10^9 years but probably several hundred million years, since the Earth was formed 4.5×10^9 years ago and the earliest evidence of life is in rocks 3.5×10^9 years old (*17*). We have measured the rate of deamination of aspartic acid as a function of pH (Fig. 1) between 60° and 135°C (*18*). Only deamination of aspartic acid was observed; there was less than 0.2 percent decarboxylation to α- or β-alanine. The equation for the deamination half-life between pH 5 and 8 is

$$\log t_{\frac{1}{2}} \text{ (years)} = -22.01 + 8048/T$$

giving 28×10^6 years at 0°C and 96,000 years at 25°C. The half-life for the deamination for pH values greater than 10 is given by

$$\log t_{\frac{1}{2}} \text{ (years)} = -17.35 + 6249/T$$

The half-lives are 330,000 years at 0°C and 4100 years at 25°C.

There is a similar deamination of asparagine to fumaramic acid at neutral pH (*19*), the rate of which is 190 times faster than the aspartic acid deamination rate at pH 8 and 60°C (*18*). The rate of deamination of the nitriles of aspartic acid should be even faster. Since the probable prebiological precursor of aspartic acid is the dinitrile, the rate of deamination during the four hydrolytic steps to aspartic acid would be very rapid in the absence of ammonia.

β-Methyl aspartic acid, which does not occur in proteins, also deaminates (*20*):

$$\text{DL-}\beta\text{-methyl aspartate} = \text{mesaconate} + NH_4^+, \quad K_{25°C} = 0.12$$

β-Methyl aspartic acid may be absent from proteins either because it is not functional or because it was not available in the primitive ocean. Since the maximum concentration of NH_4^+ allowed by the clay minerals is $0.01M$, the maximum ratio of β-methyl aspartic to mesaconic acid is 0.08. β-Methyl aspartic acid has not yet been synthesized in any prebiological experiment, but even if it was synthesized on the primitive Earth most of it would have deaminated to mesaconic acid. Preliminary experiments indicate that this deamination is comparable in rate to deamination of aspartic acid.

A single example of a NH_4^+-dependent equilibrium or prebiological synthetic pathway cannot by itself demonstrate that the concentration of NH_4^+ was greater than $1.0 \times 10^{-3}M$. However, a number of such reactions would form a more convincing argument. Another example is the synthesis of amino acids and hydroxy acids by the Strecker and cyanohydrin syntheses from an aldehyde, HCN, and NH_3. Only hydroxy acids are obtained in the absence of NH_3, and only amino acids at high concentrations of NH_3. Preliminary data indicate that the NH_4^+ concentration must be greater than $10^{-3}M$ for production of equal amounts of amino acids and the corresponding hydroxy acids at pH 8.

From the value of NH_4^+ obtained from the clay mineral or the aspartic acid–fumaric acid equilibrium, the pNH_3 and pH_2 in the atmosphere can be calculated provided the pH and the temperature are known. The equilibrium values of NH_4^+, NH_3, pNH_3, and pH_2, with the atmosphere and the ocean at the same temperature, are given in Table 1 for pH 8 and $pN_2 = 1$ atm. These values are calculated from the ionization of NH_4^+ (*21*), the volatility of NH_3 (*22*), and the equilibrium constant for the reaction (*23*)

$$\tfrac{1}{2} N_2 + \tfrac{3}{2} H_2 = NH_3$$

Equilibrium would be attained for the ionization of NH_4^+ and the exchange of NH_3 with the atmosphere and ocean. The extent to which N_2, H_2, and NH_3 approached equilibrium is a much more complicated problem, since this is a pressure-dependent equilibrium, and the ultraviolet flux would tend to decompose the NH_3, giving a steady-state concentration less than the equilibrium value. To maintain the calculated pNH_3 and in turn the NH_3 and NH_4^+ in the ocean, the pH_2 would have to be substantially greater than the equilibrium value, possibly by several orders of magnitude.

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