lie at the root of many interesting catalytic chemical reactions, some of which were used in industry even before the unique properties of hydride complexes, which formed their basis, had been realized.

This article surveys the history, preparations, important properties, and reactions of hydride complexes, surveys their part in important catalytic industrial processes, and speculates about their possible role in the biological fixation of nitrogen.

References and Notes

1. Ligands are atoms or molecules capable of direct chemical bonding to a metal ion. In $[MH_xL_y]$, H is also a ligand, formally treated as H^-; L represents a great variety of chemical groups, such as chloride ion, the cyclopentadienyl anion, ammonia, triphenylphosphine, and aromatic and unsaturated hydrocarbons. The following abbreviations are used in the article: Bu^n, normal butyl; Et, ethyl; en, ethylenediamine; Me, methyl; Ph, phenyl; phen, *o*-phenanthroline; Pr, propyl; py, pyridine.
2. Because of limitations of space, this summary is necessarily incomplete. For detailed information and all except historical or very recent references, see A. P. Ginsberg, *Transition Metal Chem.* **1**, 111 (1965); see also J. Chatt, *Proc. Chem. Soc.* **1962**, 318 (1962), and M. L. H. Green and D. J. Jones, *Advan. Inorg. Nucl. Chem.* **7**, 115 1965).
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Atmospheric and Hydrospheric Evolution on the Primitive Earth

Both secular accretion and biological and geochemical processes have affected earth's volatile envelope.

Preston E. Cloud, Jr.

This discussion focuses on the interactions that necessarily took place between biospheric, atmospheric, lithospheric, and hydrospheric evolution on the primitive earth and perhaps the moon. How can evidence and conjecture about each of these different kinds of evolution limit or illuminate hypotheses about the others, and how can all such lines of thought be integrated to bring us closer to a consistent and plausible model of early terrestrial events?

A salient and long-appreciated aspect of the terrestrial atmosphere is its great depletion in the noble gases, relative to their cosmic abundances (*1*). This seems to require the conclusion that the atmosphere as we know it is of secondary origin. Either the earth originated without a primary atmosphere, or such an atmosphere was mainly lost in a subsequent thermal episode.

Actually, an internal source for our atmosphere as a result of gradual, episodic, or rapid volcanic outgassing and weathering was proposed long before the depletion in noble gases was recognized. The Swedish geologist Högbom (*2*) suggested this in 1894, and his countryman Arrhenius (*3*), in 1896. Later Chamberlin (*4*) recognized a post-accumulational generation of the atmosphere from occluded gases as a necessary consequence of his and Moulton's planetesimal hypothesis for the origin of the earth. Rubey's critical and comprehensive assessment (*5*) of possible sources for the volatiles that comprise the atmosphere and hydrosphere has led to wide acceptance of the concept of accumulation of both from juvenile sources.

As far as the atmosphere is concerned, dispute focuses on the composition and time of origin of the primitive atmosphere and the original proportions and changes in the proportions of O_2, N_2, CO_2, and H in it.

The atmosphere cannot be older than the earth. Hence an outside limit on its time of origin is the time of origin of the earth. Much evidence has been adduced in recent years, based on the ages of meteorites (*6, 7*) and on isotopic composition of terrestrial leads (*7, 8*), to suggest that both meteorites and leads were involved in some kind of homogenization event about 4.6×10^9 years ago (10^9 years is hereafter referred to as an aeon). Small excesses of xenon-129 in some meteorites (*9*) support the inference that this event closely approximates the time of origin of the solar system and hence the approximate time of formation of the earth. Such an interpretation, however attractive and highly probable as it seems, is not the

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only possible one. On the one hand, available evidence does not completely eliminate the possibility that the earth as a solid body in the general form we know it might be as much as an aeon younger than the parts from which it accumulated (*10*). On the other hand, Baranov (*11*) suggests ways of looking at the lead isotope data which *might* require as much as 7.5 aeons for the radiogenic lead isotopes to reach current crustal ratios.

A minimal age for the earth is, of course, given by the most ancient minerals dated. This age appears to be around 3.5 to 3.6 aeons. Zircons from gneisses in Minnesota show uranium-lead isotope ratios which, on a concordia curve, indicate an age of 3.5 aeons (*12*). Amphibolites from the central Ukraine are said to give potassium-argon ages exceeding 3.5 aeons (*13*). Granites which are apparently not the oldest in South Africa (*14*) yield rubidium-strontium ages of 3.2 aeons or more, and some pegmatites give whole-rock ages as great as 3.4 aeons (*15*), although the larger figures are very uncertain. The basement complex of the Congo is said to yield lead-isotope ages approaching 3.3 to 3.4 aeons (*16*). And in Western Australia, rubidium-strontium ages indicate that granites and greenstones were metamorphosed 2.7 aeons ago (*17*) and probably originated 3 aeons or more ago (*17, 18*). Thus the earliest dates so far obtained in the rather intensively studied older parts of North America and Europe are remarkably close to each other and are approached by the ages of the oldest dated rocks in the Southern Hemisphere. Although the record is distressingly sparse, it underscores the question: What was happening for the first aeon or so of the earth's history, if accumulation of the earth was completed not long after the homogenization event that took place approximately 4.6 aeons ago? We will return to that question, and to the fact that a later marked uranium-lead differentiation, presumably denoting a significant episode in crustal evolution, is dated at about 3.5 aeons (*7, 19*)—coincidentally, about the same age as that suggested by the regrettably sparse record of dated minerals in the most ancient rocks.

The immediate point is that, inasmuch as we do not have rocks known to be older than about 3.5 aeons, geology can as yet do little to place limitations on conjecture about the nature and time of origin of an atmosphere or hydrosphere that might have existed before that time. Indeed, these oldest dated rocks have only an indirect bearing on the questions before us, and the ages obtained for them may well date only an early episode of metamorphism and not their time of primary origin.

Table 1. Stromatolites of large amplitude.

Approximate amplitude (m)	Approximate age (10^9 years)	Geologic unit	Locality
5	> 1.1	Belt Series, Helena Dolomite	Helena, Montana
6	(Proterozoic)	Otavi Series, Abenab Formation	Kombat Mine, South-West Africa
2.5–3	> 2	Dolomite Series	Boetsap, South Africa
2.5–3	1.5–1.7	Paradise Creek Formation	Northwest Queensland

Some Limitations on Conjecture

What are the oldest rocks that tell us something reasonably unequivocal about the existence and nature of the contemporaneous hydrosphere and atmosphere? They are sedimentary rocks, considered from several lines of converging evidence to have a minimum age of about 3 aeons in South Africa and Swaziland (*15*), to be more than 2.7 aeons old in Minnesota (*20*), and mainly younger than 2.5 to 2.7 aeons at other places. These rocks consist of water-laid detrital and chemical sediments that clearly could not have originated without the prior existence of atmospheric weathering and a substantial hydrosphere (see *21* for questionable older records).

As Holland (*22*), Abelson (*23*), Cloud (*24*), and others cited by them have pointed out, these rocks and associated minerals also place limitations on conjecture about the composition of the atmosphere beneath which they were deposited. Apparently detrital uraninite and pyrite at various localities combine with more esoteric geochemical evidence to indicate that the atmosphere before 1.8 to 2 aeons ago could have contained little or no free oxygen. The abundance of bedded chemical silicates, representing the chert component of the banded iron formation, and the relative rarity of limestone and dolomite among the oldest sedimentary rocks also imply that there could have been little ammonia in the atmosphere of those times. For ammonia would raise the *p*H of the hydrosphere and favor an abundance of carbonate rocks and a rarity of bedded chert. Abelson (*23*), moreover, has shown that, in an atmosphere devoid or nearly devoid of free oxygen, the dissociation of methane, had it been abundant, should have given rise to a rain of carbon of nonvital origin; yet carbon, although not uncommon, is not a conspicuous component of the oldest sediments. Thus it may be concluded that the atmosphere, from about 3 aeons onward at least, was not, as some have suggested, rich in methane or ammonia. The sedimentary record, rather, supports Rubey's conjecture (*5*) that the early atmospheric gases would be those which are occluded in igneous rocks, or which on other grounds are recognized as juvenile components of volcanic and hot-spring gases. These are H_2O, CO_2, CO, N_2, SO_2, HCl, and a few other trace gases.

Possible Timing and Significance of Postaccumulational Melting

How far back might such an atmosphere go? How would its accretion have become initiated? And what can we postulate about its evolution from the known records of biospheric and lithospheric evolution? Here we will become involved with some paleontologic and geologic evidence bearing on the appearance of the moon in orbit around the earth, not because the evidence for a postaccumulational melting episode depends on this, but because there could be a relation between these phenomena and it is interesting to examine that possibility.

In order for an atmosphere and hydrosphere to begin to accrete on an earth which, during accumulation, probably had an outer temperature of no more than a few hundred degrees Kelvin, some significant part of the outer shell or mantle of that earth would have had to undergo melting sufficient to start release of its volatiles to the surface. Such melting might have resulted from either or both of two postulated thermal episodes. One is the combined effect, early in the earth's history, of the normal evolution of radiogenic energy and the conversion of gravitational energy to heat. The other is the generation of heat from tidal friction incident to lunar capture (*25–28*), abetted by the two other factors.

Direct geologic evidence, we have seen, as yet tells us little about the nature of the earth and its enveloping hydrosphere and atmosphere before about 3 aeons ago. However, if we could find among the older rocks or fossils some that provided clues as to tidal amplitudes, this information would have a bearing on whether or not the moon might have been in orbit at any particular time. Such data, then, would constitute a test as to whether it would be consistent with the geologic record to hypothesize that lunar capture might have stimulated an early pulse of melting and outgassing, as Singer (*27*) has suggested.

Such fossils and rocks do, in fact, exist. They include the variously shaped but often domal sedimentary structures of algal origin known as stromatolites, plus various cross-bedded and desiccation-cracked sediments indicative of extensive tidal-flat deposition. The stromatolites are the most impressive evidence bearing on tidal amplitude for rocks up to somewhat more than 2 aeons old.

Stromatolites in process of formation are known from recent intertidal and shallow subtidal environments of Western Australia (*29, 30*), the Bahama Islands (*30, 31*), and Bermuda (*32*). From the few records known in modern seas, it seems that subtidal stromatolites characteristically take the form of undulating crusts and small nodules. Stromatolites that rise conspicuously above the surface on which they grow have so far been found only in the intertidal environment, where they reach a maximum known relief among recent forms of 0.7 meter in Western Australia. Logan (*29*) found that the height at maturity was "determined by the tidal range and the position of the structure in the intertidal zone." If this is true generally it would give us important clues to tidal ranges in the geologic past.

We are not entirely limited to analogy with present structures. Stromatolites in the geologic past are commonly associated with interstitial breccias and oölites suggesting turbulent waters, and with contraction-cracked sediments and truncated flat-topped ripple marks implying exposure to the atmosphere. Indeed some stromatolitic domes from 2-aeon-old rocks in South Africa (Schmidts Drift, northeastern Cape Province) show polygonal patterns of desiccation cracking on their own planed-off upper surfaces. The geologic record is thus consistent with their characteristic habitat being an intertidal one. It is also a feature of the geologic record that stromatolites of pre-Paleozoic and even early Paleozoic age often have far greater heights than do younger ones, and over areas far too extensive to represent abnormal local tidal ranges. If stromatolites, however, are to give us useful clues to ancient tidal amplitudes, we must be careful about what we measure. Some stromatolitic domes build up through the rock section. We should measure only the demonstrable height of a particular unit structure above a related bedding surface, or, better yet, the amplitude of a particular upwardly convex and complete stromatolitic lamina above the surrounding contemporary sea floor. If the characteristic habitat and manner of growth are correctly understood, this then implies, for such stromatolites, that tidal amplitude at a given time and place was at least as great as the amplitude of individual stromatolitic laminae.

What are some of these stromatolite amplitudes? I had observed that stromatolites of large amplitude were widely distributed in the pre-Paleozoic long before it occurred to me that it might be significant to keep a careful record of such measurements. A great many pre-Paleozoic stromatolites, however, have amplitudes, above the growing surface, of a meter or more. Four occurrences that show amplitudes from 2.5 to 6 meters or more and have stratigraphic associations that convey little likelihood of locally exceptional tidal ranges are listed in Table 1. These stromatolites are found in dolomites and limestones ranging in age from about 1 to more than 2 aeons, and it seems likely, from my own field reconnaissance and scanning of published accounts, that concerted effort would reveal other, similar records in this age range on all continents where such rocks occur. In addition, extensive deposits of muddy siltstone and shale of the same general age show polygonal patterns of desiccation cracking and truncated ripple marks indicative of equally extensive tidal-flat deposits (the Belt and Grand Canyon Series, for example). The giant individual stromatolite domes in the Belt Series near Helena, Montana, are illustrated by Knopf (*33*, p. 85), who describes them as "up to 15 feet thick [that is, in amplitude] and traceable for thousands of feet along the strike . . . from the bottom to the top of the Helena dolomite," a unit more than 1200 meters thick.

The implication I draw from this and other records is that tidal amplitudes too great to be accounted for by the solar component alone existed at least 2 aeons ago, that tides generally were probably greater then than they are now, and that the moon was, therefore, at that time already in orbit and presumably somewhat closer to the earth than it is now. This timing, of course, is contrary to some theoretical expectations and to recent reports, such as that of Olson (*34*), suggesting that sedimentary textures in younger rocks call for lunar origin in more recent times.

Stromatolites of large amplitude (about 2 meters) in ankeritic dolomite at Steeprock Lake, Ontario, may give a record of large tides of even greater age. Although not radiometrically established, geologic relations suggest that the age of these rocks may approach 2.5 aeons. The evidence of the approximately 3-aeon-old (*15*) rocks of the Swaziland System is even more tenuous, but also consistent with the moon's then being already in orbit around the earth. This succession of rocks, beginning with a typical, and the oldest known, marine ophiolitic and eugeosynclinal succession, is terminated by the Moodies Series of characteristic molasse facies (*35*). This includes an abundance of markedly cross-bedded and ripple-marked sandstone and conglomerate sheets, and desiccation-cracked shales. The association implies extensive intertidal deposits and again points to tidal amplitudes too great to be explained by the solar component alone (although, like most of these older pre-Paleozoic records, it needs more study from this aspect).

If the moon was in orbit 3 aeons or more ago, and if it did not originate concurrently with the accumulation of the earth, perhaps its origin had something to do with the thermal event of 3.5 to 3.6 aeons ago suggested by the oldest known metamorphic and granitic rocks and the lead isotope composition of various minerals (Fig. 1).

If our moon was captured, as is suggested by its density (*36*, p. 143) and the inclination of its orbit (*36*, p. 124), tidal friction sufficient to induce subcrustal melting would have been likely (see *26*, pp. 772–780, for a review of the theories; *36–38* for general background). Indeed, the theoretical problem is how to avoid vaporization of the earth and concomitant disintegration of the moon. Singer (*27, 28*) has suggested how such events might be circumvented, by postulating capture in a prograde rather than a retrograde orbit. This would extend the initial spin period of the earth to

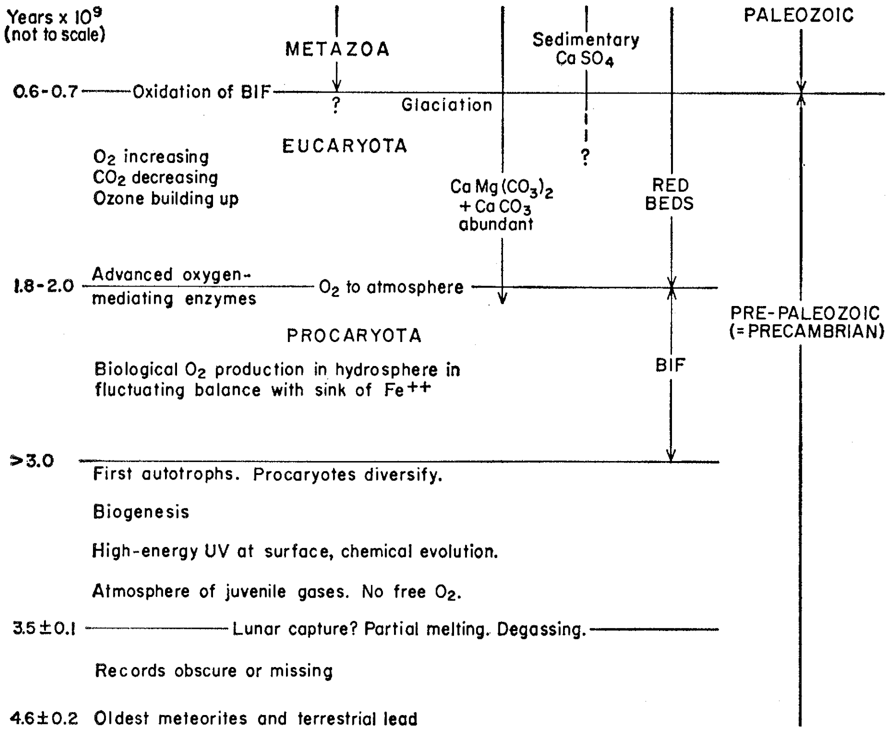

Fig. 1. Postulated main features of interacting biospheric, lithospheric, and atmospheric evolution on the primitive earth.

about 5 hours (rather than less than 1 hour) but still produce enough melting to generate a considerable concurrent accretion of atmosphere and hydrosphere. Likely related consequences for lithospheric evolution would include large-scale volcanism, plutonism, and metamorphism of preexisting cosmic debris (and of any preexisting volcanic and sedimentary rocks) as well as the general resetting of nuclear decay series.

Thus the limited chronology of the oldest rocks, and the hints from lead isotope data of the concomitant beginning or peaking of internal differentiation of the earth, can be seen as consistent with a near approach of the moon to the earth about 3.5 to 3.6 aeons ago. What little is known about lunar evolution also seems to be consistent with such an interpretation (although by no means proof of it). Just as the oldest terrestrial rocks, and conceivably the initiation or climaxing of core and mantle formation, may be related to processes incident to lunar capture, so also may the surfaces of the lunar maria, indicating as they do, from observations by Shoemaker (*38*), a welling-up from beneath to a "nearly common level." What would account for such a widespread welling-up to fill the presumably collisional maria and some smaller preexisting impact craters (for example, Archimedes) to "an approximately hydrostatic level" (*38*)? This would seem to require both a major episode, or a sequence of related episodes, of partial internal melting and a widely interconnected series of conduits along which molten or fluidized particulate matter could travel to such a nearly general level. In the absence of a core or other evidence of major internal differentiation of the moon, tidal friction provides a source of heat for fluidization otherwise difficult to visualize. In addition, stresses incident to capture might well account for an extensive interconnected lunar fracture system, along which lava, ash, or both, could ascend [as well as the impacting masses that produced the maria (*27*, *28*)]. Difficulties arise in trying to explain the preservation of large-scale relief in the lunar highlands, the absence of surface offsets due to faulting, and the lesser relief within the maria themselves. If a major melting episode did occur as postulated, it could not have been a general liquefaction of the interior of the moon nor could it have been narrowly synchronous at all places. Something more like a pervasive partial melting is called for. Interconnecting fractures along which effusive matter would have traveled outward cannot have had large offsets. And results of statistical treatments suggesting high relief within the maria (*39*) would require some other explanation. These difficulties circumscribe the model envisaged. Like it, they must undergo further critical examination, hopefully with more abundant and better evidence.

The rocks we now know cannot of themselves tell us *how* the moon originated. Among hypotheses available to choose from, however, the testimony that can be wrung from the rocks is consistent with Singer's suggested prograde lunar capture and not consistent with an origin of the moon in relatively late pre-Paleozoic time. This testimony can also be interpreted as suggesting that, however the moon originated, a near approach of moon to earth may have taken place closer to 3.5 to 3.6 aeons ago than to the 4 to 4.5 aeons suggested by Singer from tenuous geochronological inferences. And, after all, a considerable pre-mare (or pre-Imbrian) lunar history would be in order to account for the extensive lunar highlands whose infrapositional relations to debris seemingly splashed from the maria imply a significantly greater age for these highlands (*38*).

A special problem that arises in connection with a date as late as 3.5 to 3.6 aeons ago for lunar capture is that of where the moon could have been stored for a whole aeon if the earth is about 4.6 aeons old. Getting things out of the asteroid belt is no longer as fashionable as it once was, but at least one piece of evidence points to such a source for the moon. This unique planetary body, with density intermediate between that of the inner and outer planets, is the most inconsistent item in the distribution of planetary densities (*36*, p. 143) unless it did originate in the asteroid belt. If it did, and if it could be transferred from the asteroid belt to the vicinity of the earth, the storage problem would vanish.

If these conjectures should happen to be correct (and they certainly have their shaky aspects), then, when samples of the mare fillings are obtained from beneath any superficial covering debris of cosmic or local origin, such samples should give radiometric ages of about 3.5 to 3.6 aeons. Another likely corollary is that any preexisting terrestrial atmosphere and hydrosphere (*21*) would have been largely lost at that time and a new or first atmosphere and hydrosphere started, with a sizable input of volatiles. At the beginning this would probably have been no more than about 10 percent of the present mass of the atmosphere and hydrosphere, however, on the basis of Rubey's calculations showing that no more than about 10 percent of the present hydrosphere can be retained as gaseous H_2O in equilibrium with even a generally molten earth. Nevertheless, a prolonged episode of accelerated degassing could have led to fairly rapid growth of terrestrial atmosphere and hydrosphere in the following few tens or hundreds of millions of years.

It is also conceivable that the postulated near approach of moon to earth and accompanying thermal episode might have given rise to a temporary lunar atmosphere and hydrosphere. Whether this might have lasted long enough for life to evolve on the moon is a question that cannot be settled until lunar sedimentary rocks are found and examined for microfossils. If such microfossils ever are found, they might well be similar to the early pre-Paleozoic microfossils now being found on earth. Thus the development of terrestrial paleomicrobiology may offer the best foundation for the search for life in lunar materials.

Inferences from Biospheric and Lithospheric Evolution

Such reflections suggest that the present terrestrial atmosphere and hydrosphere may have evolved, with additions, from one that began or underwent great increase as a result of a major thermal episode about 3.5 to 3.6 aeons ago (Fig. 1). Life as we know it, then, would have had to originate within the next few hundred million years, if we accept as evidence of once-living things the structures described by Pflug (*40*) and by Barghoorn and Schopf (*41*) from the Swaziland System. (In Fig. 1, *biogenesis* denotes simply the origin of life in the strict etymological sense of the word and not any particular theory of origin. Pirie has used the term *biopoesis* for this, to avoid the connotation that *biogenesis* once held—of life only from preexisting life. It no longer seems helpful, however, to give up a good term like *biogenesis* merely because of historical precedent, and there is now no other reason to do so.)

In any case, first life would presumably have been anaerobic in the absence of oxygen and heterotrophic (that is, dependent on external food sources) short of a highly improbable coincidence. But it could not have continued, to give rise to the observed evolutionary record, without the emergence of an organism that could manufacture its own substance—an autotroph. However many unsuccessful starts there may have been, it is clear that one start eventually did give rise to an autotroph. But what kind? Since the biochemical complexity of the chemoautotrophs suggests a late origin for them, it was probably a photoautotroph—an organism that manufactures its food by photosynthesis. And photosynthesis is the likely process whereby oxygen might eventually appear and be generated fast enough to oxidize most of the reduced substances of the hydrosphere, atmosphere, and surface of the earth and begin to accumulate as a free gas.

Only one of the three known types of photosynthesis, however, releases free oxygen, and it is unlikely that *it* was primitive. Nevertheless, oxygen-releasing photosynthesizers did arise, and when they did they would have faced the problem of disposing of oxygen in such a way as not to burn themselves up. Unless advanced oxygen- and peroxide-mediating enzymes, therefore, arose simultaneously with, or preceded, the origin of oxygen-releasing green-plant photosynthesizers, such organisms would probably have been dependent on an associated oxygen acceptor in the physical environment.

The abundance of hematitic banded iron formation (BIF in Fig. 1) among sediments deposited between about 3 and 1.8 to 2 aeons ago suggests that the available oxygen acceptor may have been the ferrous ion. Banded iron formation is a rhythmically banded chemical sediment of large, open water bodies that takes different aspects but most characteristically consists of alternating layers of iron-rich and iron-poor silica. Nothing like it of any thickness or regional extent is found in younger rocks; and younger (but not time-restricted) types of sedimentary iron deposits appear to be mainly replacement bodies of a quite different sort. The geochemical problem of the banded iron formation has been that of explaining transport of the iron in solution under oxidizing conditions, or precipitation of the iron under anoxidizing conditions. This problem, as well as that of an oxygen acceptor for the primitive green-plant photosynthesizers, is largely resolved by the concept of a balanced relationship between organisms and banded iron formation. The iron could be transported in solution in the ferrous state and precipitated as ferric or ferro-ferric iron upon combining with biological oxygen. The rhythmic banding could result from a fluctuating balance between oxygen-producing biotas and supply of ferrous ion. The facies of iron formation can be visualized as incidental products of this regime. The oxygen presumably became locked in chemical sediments precipitated from the hydrosphere and did not appear in the atmosphere except for small quantities from photolytic dissociation of H_2O and CO_2, rapidly scavenged by reduced substances then abundant in the atmosphere and at the surface of the lithosphere.

Eventually, however, efficient oxygen- and peroxide-mediating enzymes did arise, and when that happened the postulated balance would have collapsed. Green-plant photosynthesizers, equipped with such enzymes, could then spread as widely through the hydrosphere as light penetration and high-energy ultraviolet (UV in Fig. 1) shielding mechanisms would permit. The hydrosphere would be swept free of ferrous ion in a last great episode of banded iron formation. And O_2 would accumulate in excess in the hydrosphere and begin to evade to the atmosphere. The last great episode of banded iron formation, about 1.8 to 2 aeons ago, may mark such an event, and blue-green algae are known to have been associated with it.

What would happen when O_2 began to evade to the atmosphere? At that time, in the absence of an ozone screen, ultraviolet light in the range of 2000 to 2900 angstroms would impinge on the surface of the earth, some of the molecular oxygen (O_2) would be converted to atomic oxygen (O) and ozone (O_3), and iron would be retained in the weathering profile of the earth in the ferric state. Because of the high chemical activity of O and O_3, even a low rate of evasion of O_2 to the atmosphere should give rise to a high rate of oxidation of surface materials. Red beds—detrital continental or marginal marine sediments in which the individual grains are coated with ferric oxides—should appear in abundance in the geological column at that time.

Available records indicate that the oldest thick and extensive red beds are about 1.8 to 2 aeons old—a little younger than, or overlapping slightly with, the youngest banded iron formation. The evidence of lithospheric evolution suggests that this may mark the time in atmospheric evolution when free O_2 began to accumulate, perhaps following the appearance of advanced oxygen- and peroxide-mediating enzymes in biospheric evolution.

This would also set the stage for the appearance of a new type of cell and organism. Paleontological evidence (*24*) implies that until then all organisms were procaryotes, having no nuclear wall or clearly structured chromosomes, and being incapable, therefore, of mitotic cell division and sexual reproduction in the usual sense. The presence of free oxygen, even in small quantities, was presumably followed by the evolution of the eucaryotic cell, with nuclear wall, well-defined chromosomes, mitotic cell division, and the capacity for sexual reproduction. (The oxygen requirements of a single eucaryotic cell, to be sure, are much more easily satisfied than those of a differentiated multicellular animal.)

How fast did O_2 accumulate in the atmosphere once it began? Probably slowly at first. The green-plant photosynthesizers would still be restricted by high-energy ultraviolet radiation to protected sites in stromatolite-forming sedimentary mats, or at locations where they would not be circulated into surface waters, until such time as ozone built up to a sufficient density to exclude DNA-inactivating radiation in the neighborhood of 2600 angstroms. Berkner and Marshall (*42*) found that this happens when the atmospheric level of oxygen reaches about 1 percent of the present level. In addition, both they and, earlier, the Canadian biologist Nursall (*43*) suggested that the appearance of the Metazoa (differentiated multicelled animal life) was a consequence of the reaching of atmospheric oxygen concentrations sufficient to support a metazoan level of oxidative metabolism.

Certainly the appearance of the Metazoa in the geologic record does signify the previous fulfillment of two necessary if not sufficient preconditions. One is the origin of the eucaryotic cell, of which all metazoans are constituted. The other is a sufficient level of free oxygen—although perhaps closer to 3 percent of the present atmospheric level than to 1 percent (better data on this are needed). Now the oldest rocks in which eucaryotic fossils are known are probably more than 0.7 aeon old (*44*), although the minimal conditions necessary for primitive eucaryotes may have appeared much earlier (*24*). At least the precondition of the eucaryotic cell, therefore, was satisfied well before the dawn of the Paleozoic; and I have elsewhere (*24*) provided documentation for the conclusion that there are as yet no records of unequivocal Metazoa in rocks of undoubted pre-Paleozoic age.

This, then, can be interpreted as suggesting that the precondition of sufficient free oxygen may have been the triggering event. The necessary compression of early metazoan evolution may be partially explained by postulating a polyphyletic origin. This can be visualized as a wave of multicellularization affecting different pre-metazoan ancestors almost simultaneously in the geological sense. Since, moreover, all ecologic niches that could ever be occupied by Metazoa were unoccupied when the Metazoa first arose, adaptive radiation probably contributed to a geologically rapid diversification of the metazoan root stocks. This may have taken place over an interval of, say, 100 million years, more or less—perhaps somewhat less than the time required for chemical evolution leading to the origin of life itself, and somewhat more than that required for the Cenozoic diversification of the mammals following extinction of the dinosaurs.

Is there evidence other than the geologically rapid evolution of the earliest Metazoa at this time to suggest that the dawn of the Paleozoic might indeed have closely followed the appearance of a level of free O_2 adequate for metazoan metabolism? First consider what might happen when ozone reached a level sufficient to exclude the DNA-inactivating ultraviolet radiation at about 1 percent of the present atmospheric level of O_2. As Berkner and Marshall recognized (*42*), this would open up the surface waters of the entire hydrosphere to occupation by photosynthesizing phytoplankton, and such occupation, in turn, could lead to rapid and large increase in the amount of O_2 in the atmosphere. Such a step-increase in atmospheric O_2 might be related to three features in lithospheric evolution — late pre-Paleozoic glaciation, oxidative enrichment of the banded iron formation to produce high-grade ores, and the appearance of thick and extensive deposits of sedimentary calcium sulfate in the geologic record.

Inasmuch as the increase in O_2 would presumably have been paralleled by a decrease in long-radiation-reflecting CO_2, this could have led to a temperature decrease that might have triggered the widespread late pre-Paleozoic glaciation often suggested to account for certain rocks of that age having resemblance to deposits of modern and Pleistocene glaciers (another matter needing more study).

Enrichment of the emerged banded iron formation by surface oxidation during late pre-Paleozoic or earliest Paleozoic time converted the lean primary deposits into the bonanza ores that were first mined in the Lake Superior region. This event also would be consistent with a substantial contemporaneous increase in the amount of oxygen in the atmosphere, and it may have coincided with similar oxidative enrichments in other regions to denote a broadly contemporaneous episode of surface oxidation and laterization in late pre-Paleozoic or earliest Paleozoic time.

The record of sedimentary calcium sulfate may also be consistent with the postulated late pre-Paleozoic increase in O_2. Thick and extensive deposits of gypsum and anhydrite require large amounts of sulfate ion, and the only likely adequate sources are from the oxidation of sulfides and sulfurous volcanic gases (SO_2, SO_3, H_2S). Sedimentary calcium sulfate is abundant from the base of the Paleozoic onward, yet occurrences of appreciable volume appear to be rare in, or absent from, all but perhaps the uppermost part of the pre-Paleozoic (*24*). Anhydrite in the Grenville, for instance, could be a later replacement of a tabular marble body (*45*). The most likely candidates yet proposed for thick and extensive pre-Paleozoic sedimentary sulfates are deposits in the Shaler Group of arctic Canada (*46*), although they appear to be very late pre-Paleozoic indeed (*47*, p. 55). On balance it seems that the appearance of abundant sedimentary sulfates in the geologic record may precede by only a little the origin of the Metazoa, and that both, together with oxidative enrichment of the iron protores and a reputed episode of glaciation, could be partial consequences of a relatively large-scale increase of free O_2.

The relative abundance of limestone and dolomite among the younger pre-Paleozoic rocks, as contrasted to their near absence from sequences older than about 2 aeons, may, in turn, reflect a gradual diminution of CO_2 and increased *p*H of the hydrosphere, accompanying the relatively slow buildup of O_2 in the atmosphere after it began to accumulate but before ozone reached effective ultraviolet-screening levels.

These are the kinds of things we can

postulate about the composition and evolution of the primitive atmosphere by calling on the combined evidence of biospheric and lithospheric evolution.

The Hydrosphere

As for the hydrosphere, there is little to add to what Rubey (*5*) has already so brilliantly developed. On grounds of the occasional occurrence of glauconite in rocks as old as 1.2 to 1.5 aeons (*48*)—glauconite being a mineral characteristic of the diagenesis of various siliceous and claylike parent materials in contact with potassium-rich solutions—the hydrosphere is presumed to have had saline components at least that long ago. The prevalence of dolomite among rocks as old as 2 aeons also implies normal marine to hypersaline environments at least that far back. The evidence of the older rocks is less clear; but the occurrence of sedimentary siderite, sulfide-rich sediments, bedded chert, and so on, is consistent with the presence of a hydrosphere not drastically different in its *p*H and mix of dissolved salts from the present one. The *Eh*, at least before about 2 aeons ago, was probably negative or neutral, however, and the *p*H may have been slightly lower than now. Sulfate ion was apparently present in solution only in quantities too small to account for much $CaSO_4$ until the latest pre-Paleozoic.

Evidence that might suggest nonsaline seas includes the interesting fact that, among the commoner elements of the microbiotas now being found in rocks of various ages in the pre-Paleozoic, many are morphologically close to living freshwater forms. Such organisms, however, are characterized by a combination of morphological conservatism and ecological plasticity. Similar living forms tolerate a wide range of salinity. Their pre-Paleozoic ancestors probably lived in salt water. The iron formation itself, however, has been taken as evidence of a freshwater environment. That is because iron in modern marine waters occurs only in vanishingly small quantities. Under anoxygenous conditions, though, dissolved ferrous ion could have been, and evidently was, relatively common in older pre-Paleozoic seas of approximately normal salinity, and probably of a range of *p*H and temperature not greatly different from the range for younger seas.

There remains the question of the configuration of the pre-Paleozoic hydrosphere. If, as suggested, it accumulated gradually, while the continents and ocean basins were still differentiating, the main part of it may in early times have occupied isolated basins of intermediate depth rather than deep interconnected ones, such as comprise the present world ocean. If this was the case, the sequence and timing of events postulated might have varied from one basin to another. The record as now understood does not support such a variation, but differences in the range of tens of millions of years are not yet resolvable in pre-Paleozoic time. Among the many unfinished jobs ahead for geologists, one of the most important is to map and date the shorelines and to estimate the physical structure and environments of the pre-Paleozoic sedimentary basins. When such information is available over very large regions we should be able to make better informed guesses as to the configurations, volumes, tidal range, and history of the evolving early hydrosphere and its relation to other parts of the primitive earth.

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Solid State Physics as a Source of Modern Electronics

Solid state physics leads to device effects from which electronic technology provides new tools for science.

Rolf Landauer and John J. Hall

In discussing the useful technology that has come out of solid state physics, we must first recognize that both the source field and the range of applications are broad and cannot easily be delineated. As far as the origin of useful ideas is concerned, there are no strictly valid boundaries between solid state physics on the one hand and physical chemistry, electrochemistry, physical metallurgy, and quantum electronics on the other. We are dealing with a continuous spectrum of activities concerned with the behavior of matter in condensed aggregates. The range of applications is also broad: photography and other image-formation techniques, the development of adhesives, the generation and storage of electrical power, even the manufacture of costume jewelry. Of the older applications, the development of new structural materials has offered the greatest source of ideas for the physicist. In this field we have seen many advances; for example, we now understand a great deal about stress corrosion mechanisms (*1*); we know how to imbed thin fibers of nonplastic materials into a plastic matrix to obtain strength comparable to that in ideal substances (*2*); we have learned how to use single crystals to prevent the fracture of turbine blades (*3*). These are only a few of the many examples of fundamental progress in the field of structural materials.

However, it is difficult in the older fields to separate the impact of today's physics from the natural ultrarefinement of yesterday's technology. Consider, for example, the central concept in the field of structural materials: the dislocation. The dislocation is a defect in the crystalline pattern of atomic arrangements; it explains how plastic deformation can occur in real crystals under forces much smaller than the smallest which would be expected to produce deformation in ideal crystals. The notion of dislocation requires only that a crystalline arrangement of atoms is normally present; beyond that, dislocation theory relies upon classical elasticity theory, with little need for the more recent advances of solid state physics. Indeed, the word *dislocation* has simply enabled us to replace the older notions of the metal physicists about "locked-in microstress" with a more detailed, suggestive, and precise concept. This is in no sense an adverse reflection on the importance of the idea of dislocations; the point is made here to emphasize the fact that crisp illustrations of the relevance of fundamental physics to technology can be drawn only from new fields of application. We therefore concentrate, in this discussion, on the impact of solid state physics on the largest of the new fields: electronics. And even here we select a main track and ignore many important developments—for example, light-emitting semiconductor diodes and nonreciprocal ferrite devices.

Through technology we learn to transcend the limitations of our biological endowment. The early development of tools represented man's ability to handle matter more effectively than the strength of his skin and the shape of his fingers permitted when he used only his bare hands. The use of fire, the wheel, the use of ladders—all are links in a chain which, in the 19th century, brought us into a period in which we became independent of human and animal sources of energy. Now, in the 20th century, we are learning how to handle information in ways which far transcend our ability to shout down the hallway or figure sums with pencil and paper. Our accelerating capabilities in handling information can, however, be expected to go far beyond automated bookkeeping and long-distance telephony. For example, we have started to use the computer in the schools, not only as a means of relieving the immense administrative burden but as an instructional tool which promises eventual tailoring of courses to the individual student's speed of response. Today we spend much of our energy constructing highways and airports, classrooms and office buildings, when our real aim is to transmit, exchange, and control information. We will eventually learn to eliminate the unnecessary overhead and to deal with the information. We thus foresee

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