Proceedings of the 15th Inter-University Geological Congress, 1967. University of Leicester, England.

SEDIMENTARY ORES OF THE EARLY AND MIDDLE PRECAMBRIAN AND THE HISTORY OF ATMOSPHERIC OXYGEN.

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Abstract.

The occurrence of stratified ores such as gold-uranium-pyrite reefs and banded iron formations in the Early and Middle Precambrian, and not later, proves the existence of an early anoxygenic atmosphere. As photosynthesis was an early acquirement of life, it is postulated that the oxygen level of the atmosphere was maintained at about 1% of its present value. The importance of this feature for the development of life is dicussed.

As I am neither a sedimentologist nor an ore geologist, it is not my intention to discuss the sedimentary ores of the Early and Middle Precambrian themselves. Nevertheless, they are of importance in the study of one aspect of the question of the origin of life on earth; that of the history of atmospheric oxygen.

Recent advances in thinking and experimentation about the possibility of an origin of life through natural causes have led to a general acceptance of the opinion that this can only have been possible in a primeval anoxygenic atmosphere. This view is also in keeping with the findings of astronomers since the normal atmospheres of planets and stars appear to be of a reducing character, without an appreciable amount of free oxygen (Urey, 1959; Mueller, 1963).

It has also been shown that photodissociation of water vapour, which was formerly invoked to account for our free atmospheric oxygen, becomes impossible above a certain, very low, level of atmospheric oxygen. This rests upon a set of circumstances first proposed by H.C. Urey, and further worked out by Berkner and Marshall (1966). The main factors governing this process are, first, that the shorter ultraviolet wave lengths of sunlight which dissociate water vapour are the same as those used by oxygen to combine to form ozone, and secondly, the existence of the so called "cold trap" in the higher atmosphere. The first of these factors means that any appreciable amount of free oxygen in the atmosphere will hamper dissociation of water vapour, as it competes for the energy of the same radiation. The "cold trap", an altitude of some 30 Km, effectively freezes out all water vapour, which is therefore nonexistant in the higher atmosphere above this level. Oxygen, on the other hand, is distributed exponentially through all of the atmosphere, as are most other gases. The result of this difference in distribution between water vapour and oxygen is that at 0.001 PAL (that is at 0.1% of the Present Atmospheric Level) of free oxygen,no more photodissociation of water can take place.

Berkner & Marshall (1966) rightly insist that this important self-regulatory mechanism would keep the level of free atmospheric oxygen at 0.001 PAL - a concentration level which they propose to call the Urey Level - and could not be broken by any inorganic process. The only possible mechanisms by which these conditions could be changed would be by some unknown extraterrestrial influence, supernatural intervention, or the biogenic production of free oxygen. For obvious reasons the last explanation is widely accepted, and it is now concluded that all our present atmospheric oxygen is biogenic in origin.

Once the postulated anoxygenic primeval atmosphere is accepted, the "chemical origin" of life seems entirely feasible, although the details of the process have not yet been fully worked out (Calvin, 1965; Oro, 1965).

This point established, it becomes important to postulate when organic photosynthesis could have started, i.e., when the organic production of atmospheric oxygen began. Eglinton *et al.* (1964) and other member's of Melvin Calvin's group (see Belsky *et al.*, and Johns *et al.,* 1966) have recently attained a major advance in this field by the identification of so-called "chemicofossils" or "molecular fossils" in Precambrian shales and cherts. Branched iso-prenoid alkanes, notably phytane with $N = C_{20}$ and pristane with $N = C_{19}$, which are interpreted as breakdown products of chlorophyll or of chlorophyll-like molecules, are found in beds as old as the Soudan Iron Formation, which has a minimum age of 2.8 billion years.

The existence of photosynthesis on earth does not, however, mean the existence of an oxygenic atmosphere. In the first instance, the organically produced oxygen would only replace that derived inorganically, which will be produced in lesser quantities as the organic production rises. From the breaking of the Urey Level, all atmospheric oxygen will be biogenic in origin, however, the level of free oxygen that might finally be attained rests upon the balance between production and consumption (for instance by oxidizing surface materials).

We should now consider how the geological history of the earth can be used to provide indications as to whether the theory of an anoxygenic primeval atmosphere is acceptable or not. Unfortunately, the geological evidence is scarce and vague, but we must neverthe less try to use what we have to the utmost.

It stands to reason that in this study we may neglect all igneous and (moderate to strong) metamorphic rocks. They reached their present state at some depth in the crust, and most of their earlier characters have been destroyed, or at least obscured in the process. Hence they formed without contact with the atmosphere, and were not influenced by the state of the prevailing atmosphere (Rutten, 1962 and 1964). We can only hope, therefore, to get an answer from a study of erosion products and fossil soils (if these can be detected) and from sediments. Among the latter, two groups of sedimentary ores, the pyrite-gold-uranium sands and the banded iron formation respectively, have been cited over the past years as indicative of having been laid down under an anoxygenic atmosphere. (See for the pyrite sands Ramdohr, 1958; Jenson & Dechow, 1964; Schidlowski, 1965, 1966; and, as a critic, Davidson, 1965. For the banded iron formations Lepp & Goldich, 1964; Hough, 1958 and Govett, 1966). Both types of sedimentary ores have a characteristic in common in that they only occur in the Early and Middle Precambrian and not in either the Upper Precambrian or the Phanerozoic. The division of the Precambrian followed here, is that worked out for Minnesota by Goldich et al. (1961) as it is the only one based on a sufficient insight of the succession of orogenic cycles, and on sufficient reliable absolute dates.

At first sight the case for the pyrite sands is stronger than that for the banded iron formations, for in the first group we find little or no oxidation of the sulphide grains, whereas in the banded iron formations there is evidence of some oxidation. Although it seems certain that most of the hematite in these ores is a later replacement, mainly of magnetite, and although it is held probable that there has been no primary hematite at all, the main primary minerals such as magnetite, siderite and iron silicates all indicate some degree of oxidation. An explanation which would place the formation of the pyrite sands at an earlier date than that of the banded iron formations, which then could have been formed in contact with an atmosphere possessing already a somewhat larger amount of free oxygen, is impossible. Pyrite sands and banded iron formations occur intermittently in virtually all of the old shields formed throughout the Early and Middle Precambrian.

An answer to this riddle may, on the other hand, be found by applying the following considerations. First, in sedimentation, the transported mineral grains often do nott reach equilibrium conditions before they are buried and lose contact with the atmosphere. Second, although pyrite sands and banded iron formations occur through all of the Early and Middle Precambrian, they are not contemporaneous in a given basin. Instead, each of the two belongs to a different period within its own orogenic cycle.

With regard to the equilibrium conditions themselves, we can see from Fig. 1 that a difference in the partial pressure of atmospheric O_2 has not the slightest influence on the ultimate weathering of pyrite. Even at partial pressures of 1% of the present, only the upper line of the hematite field is slightly affected. It follows that the type of sedimentation is not determined by stability fields alone, but by the balance between the rate of weathering and the rate of sedimentation. Even in our atmosphere pyrite grains are sometimes sedimented without oxidation, but only if either the rate of weathering is exceptionally slow (i.e. tundra), or if the rate of sedimentation is exceptionally high (i.e. Indus Valley). A rather drastic conclusion follows from this, i.e. that normal geochemistry, which thinks in equilibria and expresses itself in Eh/pH diagrams, is worthless when applied to this type of sedimentological question.

The orogenic cycle concept, so familiar in the Phanerozoic, and which Umbgrove has called "the pulse of the earth", has since been applied to the Precambrian also. First used by Sederholm and his school in a purely geological way in unravelling the history of the Fennoscandian Shield, it has since been corroborated by the apparent "rejuvenation" (Magnusson, 1960) of absolute dates during subsequent orogenies. This leads to a statistical bunching of absolute dates during successive orogenic periods of the Precambrian (Gastil, 1960).

If we now try to allocate both the pyrite sands and the banded iron formations to the periods within the orogenic cycle in which they were formed, it is clear that the pyrite sands belong to a post-orogenic period, the banded iron formations to a geosynclinal period. The pyrite sands, with their conglomerates, tell of rapid transport, and hence of rapid erosion in the hinterland and of rapid sedimentation in the basin. They also show a predominance of mechanical over chemical erosion. The banded iron formations, on the other hand, depend mainly upon leaching of a stable, peneplained hinterland, slow transport and sedimentation, and a predominantly chemical process, not only of weathering, but also perhaps of sedimentation. Translated into our modern oxygenic atmosphere of the Phanerozoic, the pyrite sands are the equivalent of Red Beds, the banded iron formations of cherts and limestones.

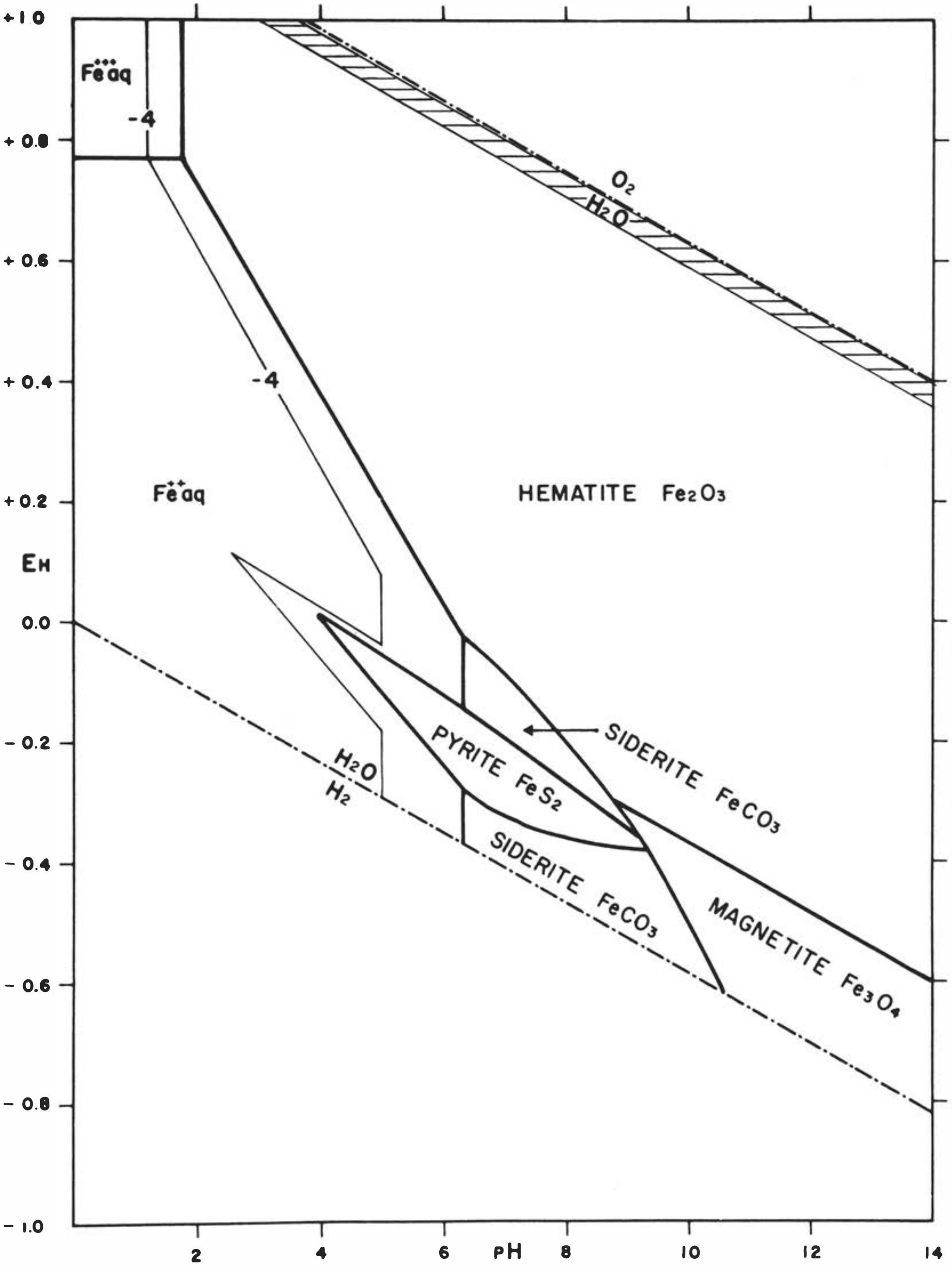

Fig. 1.
Stability fields of iron compounds in water at 25° and 1 atm. pressure. From GARRELS, 1960. The barred area in the upper part indicates the shift of the boundary between the fields of O_2 and H_2O between 1 PAL O_2 and 0.01 PAL O_2 (lower line). Such a shift does not affect the other stability fields (courtesy Dr. W. C. Kelly).

Once this deduction is accepted, it follows that throughout the Early and Middle Precambrian there was an atmosphere with very little oxygen, under which, each in its own period within successive orogenic cycles, pyrite sands and banded iron formations could develop. Owing to the present deficiencies in our geochemical knowledge, we cannot estimate the level of free oxygen in this primeval atmosphere. It is, however, possible to find an indication of this level in the present microbial world. Louis Pasteur discovered that many presentday microbes change their metabolism from fermentation to respiration at the level of about 1% of the present free atmospheric oxygen. These microbes are called "facultative aeorbes" (Stanier et al., 1963) because, in the present atmosphere they ferment under anaerobic and respirate under aerobic conditions, hence they may live either anaerobically or aerobically. In our study they could better be called "facultative respirates", because they will ferment under the primeval atmosphere, as long as its oxygen level remains below 1% P.A.L., and start to respirate when its oxygen level reaches 1% of the present.

It is postulated that this change-over from fermentation to respiration is, at least in part, influenced by thermodynamic factors, which make fermentation the more useful form of metabolism when there is very little free oxygen present. Hence it is supposed that the level of this change-over, called the Pasteur Point or Pasteur Level (Berkner & Marshall, 1968) will not have been considerably different for the microbial world of early life.

The Pasteur Point will therefore have formed another self-regulatory mechanism, which tended to keep the level of free oxygen in the primeval atmosphere at 1% PAL. For any oxygen produced over and above this level by the early photosynthetic organisms would have been immediately consumed by a change from fermentation to respiration by facultative respirators amongst the contemporaneous microbes.

At this level, we may postulate, there was not enough free oxygen to oxidize sulphides in a rapid cycle of erosion-and-sedimentation, but just enough to allow for partial oxidation of iron ions in a slow cycle. The deposition of pyrite sands and banded iron formations, consequently, will give an indication of the time during which the Pasteur Level maintained the free oxygen of the primeval atmosphere at 1% PAL. That is from at least 2.8 billion years ago to some 1.8 billion years ago.

Summing up all these assumptions, postulates and deductions, we arrive at a tentative and schematic history of atmospheric oxygen, such as presented in Fig. 2, which is, I hope, self explanatory.

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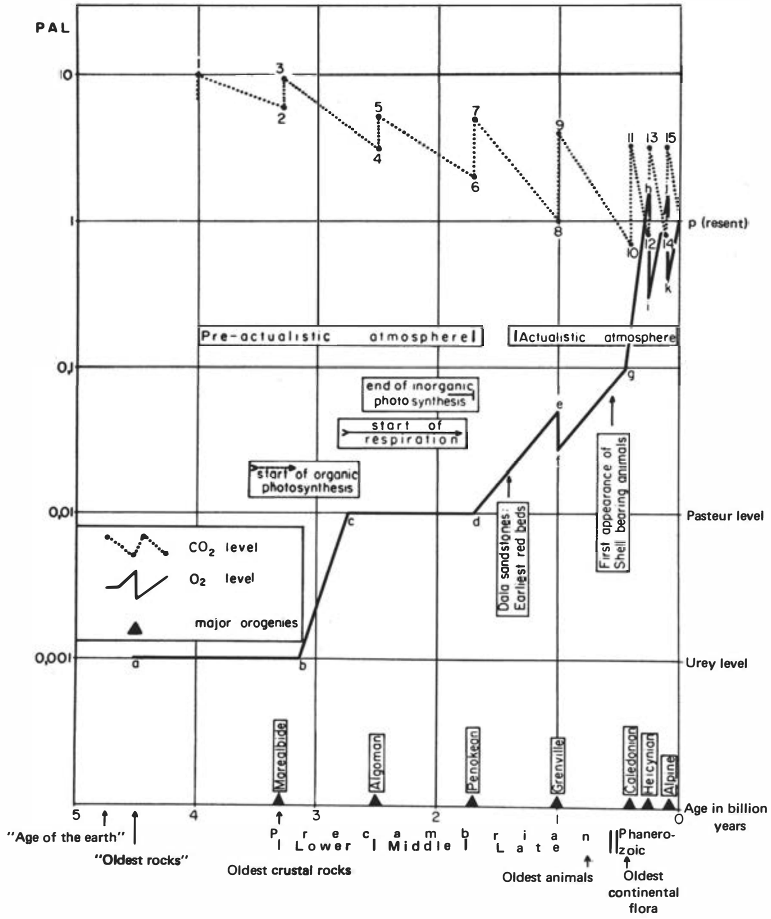

Fig. 2.

Outline of the atmospheric history of O_2 and of CO_2. Major orogenies from GASTIL (1960).

a: Oldest rocks known. O_2 is at Urey Level of 0.001 PAL.

b - c: Photosynthesis is supposed to beppresent at the time of deposition of the Soudan Iron Formation, 2.7 billion years old. The Urey Level is postulated to be broken before the Algoman orogeny. All things remaining equal, life will expand exponentially, so the amount of oxygen will also rise exponentially, as represented by the straight line between b and c.

c - d: Regulation of the O_2 level at 0.01 PAL through the influence of facultative respirators of the early microbial world is dated by the occurrence of both pyrite sands and banded iron formations.

d - g: The Pasteur Level is thought to be broken after the deposition of the youngest known pyrite sands and banded iron formations. Oxidation becomes so strong that Red Beds (Dala Sandstones) can be formed. The transition from the preactualistic anoxygenic to the actualistic atmosphere takes place.

e - f: The Grenville Orogeny, bringing much reduced material to the earth's surface is thought to lower the oxygen level temporarily.

f - g: Further photosynthesis during the long, relatively quiet geosynclinal period between the Grenville and Caledonian Orogenies leads to a further rise of the oxygenlevel, until it reaches 0.1 PAL in the Ordovician with the earliest continental flora. Somewhere along the line the oxygen level becomes high enough for the development of animals.

g - h: Strong photosynthesis by the exuberant continental floras of the Paleozoic leads to an oxygen level higher than the present.

h - i - j - k - p: Alternation of orogenic periods with stronger and geosynclinal periods with weaker oxygen consumption, leads to an oscillation of the oxygen level around the present one.

1 - 15: The CO_2 level does not have, as far as is known at present, regulartory mechanisms comparable with the Urey and the Pasteur levels for oxygen.

It is postulated that CO_2 production will be higher during the orogenic periods characterized by strong vulcanic activity, whereas during the quieter geosynclinal periods depletion through photosynthesis takes place. Because of the expansion of life with time, it is postulated that the consumption will be stronger, and hence the lines of depletion steepen in the younger periods.

10: During the long quiet period between the Grenville and the Caledonian orogenies, the CO_2 levels fall below the present one. In the ensuing (slightly) alkaline seas, animals learn to construct phosphatic and calcareous shells.

The figures given for the CO_2 level consequently are arbitrary.

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Discussion.

Professor P. C. Sylvester-Bradley (University of Leicester): Professor Rutten, you have eloquently placed before us a whole series of ingenious hypotheses concerning the origin of life. We have with us here a great variety of specialist experts, and I would like to take the opportunity to explore the possibility of devising geological tests for some of these hypotheses. One problem is to determine just when our present oxygenic atmosphere was first established. (I believe that the American Association for the Advancement of Science are, at this very moment, discussing the evolution of the atmosphere. It is a pity that we do not have their results before us). Miller early showed that "prebiological synthesis" was possible using Urey's model of a prebiological atmosphere in which methane, water and ammonia were major constituents. Since that time two other model atmospheres have been tested; one a "dry" model, with methane, ammonia and prussic acid, the other an atmosphere with a greater proportion of combined oxygen, consisting of carbon dioxide, nitrogen and water. It has been found possible to perform organic synthesis in all three of these atmospheres under abiological conditions. Can we devise a geological test to determine which model is most likely to have occurred in Precambrian time?

A second problem concerns the interpretation of what have become known as "biological markers". These are molecules of organic compounds which have been termed "chemofossils" by Calvin. At one time it was thought that they could only be produced by biological means, and their presence was taken as a certain indication of life processes at work. As an example of such chemofossils we have the isoprenoid alkanes, pristane and phytane. These have been found in many geological situations which are regarded as certainly biological (e.g. the Green River Shale). However, they have also been found in all Precambrian sediments in which alkanes occur, and even in many meteorites. Now Calvin has described how they can be produced abiogenically in an industrial process ("Molecular Palaeontology" – *Trans. Leicester Literary & Philosoph. Soc. Vol LXII* pp 45-69, 1968), and Oro has reported their abiogenic synthesis in the laboratory using iron from the Canyon Diablo meteorite as a catalyst. In fact, quite a large number of these so-called "biological markers" have now turned up in abiological environments, and it no longer seems certain that we have evidence of life when these are found in carbonaceous chondrites or in early Precambrian sediments.

Finally, there is a question I would like to ask you about the possibility of life not having originated in open water. If the prebiological atmosphere allowed the passage of ultra-violet light, open water would have been inimical to life. It would seem to me that life more probably originated among bottom sediments of coastal regions, shielded by the mud from ultra-violet radiation. Another possible location would be in ground-water. I believe that all ground waters investigated have been found to carry an extensive microflora. Perhaps this little investigated environment was the seat of the origin of life.

Professor Rutten: With regard to your first question, I am unable to think of a possible geological test to chose between your three models of pre-biological, i.e. inorganic, synthesis of "organic" compounds, except that in the case of your third model the arguments of Sillen, Holland and others seem to rule out a primeval atmosphere in which the amount of carbon dioxide was much higher than in the present one.

The models mentioned by you are, of course, not the only ones possible and I have the impression that inorganic synthesis of "organic" compounds could have occurred in a large number of quite varied environments, and that various kinds of energy could be used, if and when the primeval atmosphere was anoxygenic.

As to the diagnostic value of the so-called molecular fossils, it has always been agreed that inorganic synthesis of such compounds is possible under an anoxygenic atmosphere. The evidence lies, however, in the relative amounts of (for instance) the branched isoprenoids, such as the scarcity of the C_{18} and C_{17} species. This indicates degradation rather than synthesis. In natural synthesis one would expect a normal statistical distribution of the amounts of the compounds formed, and this is indeed what has been found in the experiments. I do not see why the aberrant results obtained in a carefully controlled and regulated industrial process - at Katazonal temperatures at that - should invalidate this line of evidence.

However, I readily concede that the concept of molecular fossils is but five years old. Further experimentation and further development of theoretical considerations will certainly supply us with a much clearer view in 50 years if not a lot sooner.

As to your last question, it seems to me entirely possible that life originated in either bottom sediments, or ground water or indeed in both. This does not, however, exclude its formation in open water. If my interpretation of the atmospheric history of oxygen is correct, pre-life and early life have been co-existant for something of the order of one billion years. During this time life could have developed from pre-life over and over again, and in various environments. However, in view of the much greater volume of environment available, and because of the better chances of mixing the various stages in the sequence of events leading from pre-life to life - Bernal's biopoesis - I personally prefer the open water environments.