GEOLOGIC DATA ON ATMOSPHERIC HISTORY

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SUMMARY

Attention is focussed on the possible existence of an anoxygenic, primeval atmosphere and on the history of atmospheric O_2 and CO_2.

For this purpose, geologic data can be divided into those on fossil remains, on biogenic deposits formed by early life, on "chemicofossils", and on deposits formed by exogenic geologic processes. Only the latter, mainly through the processes of weathering and sedimentation, give any indication of the nature of the contemporaneous atmosphere.

A tentative schematic diagram of the history of atmospheric O_2 and CO_2 is presented in Fig.1.

INTRODUCTION

Geologic data are in general open to various interpretations. This is so, because the facts, as written in the geologic record, result in most cases from a number of unrelated processes, and it is difficult to assess the influence of each of these, even on a qualitative basis. As such I don't feel myself to be very much of a stranger amidst a circle of readers which partly consists of meteorologists. But it must be remembered that even our facts are much less known than in meteorology.

In regard to studies on the composition of the early atmosphere, the geologic literature typically reflects this state of affairs. There have been wide divergencies in opinion as to the possible variations in its composition. Opinions are often based on the same factual data, but interpreted along different lines.

As an example even one of the most striking features, the atmospheric composition during the Upper Carboniferous, has not resulted in a clear picture. At that time, roughly one-quarter billion years ago, there lived an exuberant continental flora, resulting in the largest accumulation of coal seams during any geologic period.

Now, did, or did not, this proliferation of the plant kingdom result in an at-

mosphere richer in O_2, through stronger photosynthesis? At first sight the answer must be "yes". But then, it is held that the bulk of actual photosynthesis comes from oceanic phytoplankton, and it is not certain whether the continental flora of the Upper Carboniferous really produced a measurable excess. The best evidence is not quantitative, but both qualitative and circumstantial. It is not derived from the flora; not from its character, nor from its bulk, but from the contemporaneous insect world. Insects reached sizes of well over a meter during the Upper Carboniferous. In view of their primitive means of breathing, by way of trachea through the external skeleton, it is felt that these could only survive in an atmosphere with a higher O_2 level.

As a geologist, the author is quite satisfied with this line of evidence, but other geologists are not. And there is no way of convincing one's opponent. This example is only cited to illustrate the state of the art. And the author would not have dreamed of using up anyone's time in a summary of similar geologic data on atmospheric history, had not, in later years, one special topic out of the whole of this history, gained special interest.

This is the question of a possible anoxygenic primeval atmosphere, and of the transition period from such anoxygenic primeval atmosphere to the present oxygenic one. The author, consequently, will limit himself to this single topic out of the whole history of the atmosphere.

Parenthetically remarked, this interest in the early atmospheric history of the earth stems from the new wave of research into a possible origin of life on earth through natural causes. Such origin seems feasible only in an anoxygenic atmosphere, and hence the search for indications of such an atmosphere in the early history of the earth (among many others, RUTTEN, 1962; CALVIN and CALVIN, 1964).

Research into the composition of the early atmosphere is then furthermore interwoven with that into the development of life on earth, because it is supposed that the bulk of the present free oxygen is biogenic in origin, resulting from the dissociation of atmospheric CO_2 through organic, vegetable photosynthesis.

CLASSES OF EVIDENCE FROM GEOLOGY

At first sight one would expect that the following groups of geologic data might supply indications of the composition of the contemporaneous atmosphere:

(1) Fossils.
(2) Biogenic deposits.
(3) "Chemicofossils".
(4) Exogenic geologic processes.

Fossils

Fossils—morphologically preserved, fossilized remnants of early life—only

supply us with the indication of a contemporaneous oxygenic atmosphere in the case of higher landplants and of animals. The first date back to the Ordovician period, some $0.5 \cdot 10^9$ years ago, the second to the late Precambrian, with an estimated maximum age of $1 \cdot 10^9$ years. Lower plants, and notably microbes, may thrive both in an anoxygenic or in an oxygenic atmosphere. As such the earliest known fossils, that date back to at least $1.6 \cdot 10^9$ years (BARGHOORN and TYLER, 1965), do not supply any evidence as to the metabolism of the primitive plants which lived at that time nor, consequently, about the composition of the contemporaneous atmosphere.

Biogenic deposits

Biogenic deposits—secretions formed by organisms, more often than not do not even tell us what organisms were responsible for their formation. A fortiori, they do not supply any information about their metabolism. They only prove the existence of life on earth. As such the early Precambrian deposits in the Dolomite Series of Rhodesia are still the most important, having been dated as older than $2.7 \cdot 10^9$ years.

"Chemicofossils"

"Chemicofossils" constitute a new group of organic remains, which became only recently known from the work of M. Calvin and co-workers (EGLINGTON, et al., 1964; BELSKY et al., 1965) are formed by stable endings of complex hydrocarbon molecules, notably the isoprenoids $C_{18}H_{38}$, $C_{19}H_{40}$ (pristane) and $C_{20}H_{42}$ (phytane). These not only prove the existence of life on earth, but also indicate its possible metabolism. As they form parts of larger molecules belonging to the chlorophyll group, they are thought to prove the existence of vegetable life forms, capable of organic photosynthesis.

Although the existence of these "chemicofossils" far back in time—that is at least $2.5 \cdot 10^9$ years ago—throws a completely new light on the development of actual life out of protobionts, this in itself is not enough to assess its influence on the composition of the contemporaneous atmosphere. For it is not only the production of free oxygen alone that counts, but the rate of production, as balanced with oxygen losses, such as through oxidation of surface minerals.

Exogenic processes

Exogenic processes are geologic processes occurring on the surface of the earth. These do not supply any evidence of the existence of life on earth. But they may give an indication about the existence of an anoxygenic or an oxygenic contemporaneous atmosphere.

This mainly implies the cycle weathering–erosion–transportation–sedimentation. Under the oxygenic atmosphere only oxides, such as quartz and magnetite, are resistant to chemical weathering. They are only attacked by the normally much slower processes of physical weathering, such as frost action or sun blast.

The result is that nowadays all sands are mainly composed of quartz. Any appreciable amount of other minerals, such as sulphides, indicates either extreme circumstances of sedimentation, resulting in rapid burial and exclusion from contact with the atmosphere, or extreme climate, prohibitive for chemical weathering.

Under an anoxygenic atmosphere only a small amount of chemical weathering will take place. All superficial rocks will be mainly exposed to physical weathering. Degradation will then vary according to hardness, not according to chemical composition. During sedimentation, grains will be sorted according to grain size and specific weight, and sands will be composed of grains of very different chemical compositions.

Such ancient superficial deposits; sands and conglomerates; consisting of grains of oxides such as quartz, of sulphides such as pyrite, and of various other components, have actually been described by RAMDOHR (1958) from Precambrian gold–uranium reefs of various ages from the old shields or South Africa, Brazil and Canada.

A similar line of evidence, but based on quite different material, has been presented by LEPP and GOLDICH (1964). These authors noted that the so-called "iron formations"—sedimentary layers of iron ore—are different in the Precambrian from those laid down during the later history of the earth. In the earlier type of iron formations, e.g., those mined so intensively on the Canadian Shield, iron and silica are closely connected. In the younger deposits, on the other hand, such as in the French "minette" ore, iron is primarily connected with calcium carbonate.

Iron formations, being of sedimentary origin, are of course influenced by the contemporaneous atmosphere. LEPP and GOLDICH (1964) calculate that under the E_h/pH conditions of an anoxygenic atmosphere and corresponding hydrosphere, solubility of iron and silica, washed out from a continental hinterland, will determine deposition in the same area, if not simultaneous deposition. Whereas under present conditions the silica will be transported much further, and iron and calcium will fall out together.

DEPOSITS FORMED UNDER ANOXYGENIC AND OXYGENIC ATMOSPHERES

Several lines of evidence from exogenic geologic processes consequently attest to the presence of an anoxygenic atmosphere during the early history of the earth. Other exogenic deposits—sediments—show strong oxidation of their components, attesting to the existence of a contemporaneous oxygenic atmosphere. Most

notable amongst the latter are the so-called "red beds". These are formed by fine-grained sands and by silts, which owe their red colour to the fact that their limited amount of iron, often a couple of percent only, is in the ferric form of hematite or limonite.

DATING OF THE TRANSITION FROM THE ANOXYGENIC TO THE OXYGENIC ATMOSPHERE

Dating of non-oxidized and oxidized sediments provisionally indicates that the youngest non-oxidized sediments are about $1.6 \cdot 10^9$ years old, whereas the oldest oxidized sediments date back to $1.2 \cdot 10^9$ years. Between these dates the transition from the primeval anoxygenic atmosphere to the present oxygenic must have taken place.

These dates greatly differ from, and occur much earlier than those arrived at by BERKNER and MARSHALL (1965). This difference is due, not to a difference in the factual data used, but to a different interpretation. As such, it is another typical example of the difficulties encountered in geology.

Berkner and Marshall's reasoning rests upon the oxygen level of the primitive atmosphere. They noted that below 0.01 PAL O_2 (PAL = present atmospheric level), life comparable to the present was only possible, when shielded by a water layer about 10 m thick. This means that before that time life could not have expanded to the oceans. For the photic zone extends only to some 40 or 50 m depth, whilst the wave basis reaches some 30 m. The early, and consequently planktonic, life would have been in consequent danger of being thrown up into the higher, lethal levels by oceanic waves.

Berkner and Marshall conclude, that before the level of 0.01 PAL O_2 was reached, life had to limit itself to deeper river ponds and to lakes, where only shallow waves could develop. After that, it could spread out into the oceans and gain both a much wider and a much more varied habitat.

This stage is placed by Berkner and Marshall at the beginning of the Cambrian, with the "explosion of life", only $0.6 \cdot 10^9$ years ago.

THE "EXPLOSION OF FOSSILS" AT THE BEGINNING OF THE CAMBRIAN

We have, however, at the beginning of the Cambrian not the "explosion of life", but—only—the "explosion of fossils". Nine out of ten of the animal phyla are represented in the Cambrian system, and there is evidence that they extend back in time considerably more (GLAESSNER, 1966).

However, the "explosion of fossils" depends not only upon the presence of life on earth, but also upon its ability to construct hard parts, such as shells. These stand a far better chance of fossilization than weak parts.

Palaeontology tells us how the construction of shells seems to have taken place more or less simultaneously, and consequently more or less independently, in various parallel evolutionary lines. Moreover, it has followed a similar development. It started with the construction of phosphate shells, which became replaced, at a later date, and in some lines only, by calcareous shells. This parallel evolution is so much in evidence, that I. M. van der Vlerk (personal communication) for instance speaks about a new fashion being introduced in the animal kingdom at the beginning of the Cambrian, i.e., the fashion of wearing shells.

Such a widespread, more or less simultaneous beginning of shell construction might well have been induced by a temporary lowering of the atmospheric CO_2 level, and have nothing to do with the O_2 level. This would lead to a change of pH of ocean waters, leading to mild alkalinity and facilitating the construction of shells.

Once this capability had been acquired, it must have been relatively easy to defend such shells, when the CO_2 level rose again. At present, for instance, fresh water mussels manage to build calcareous shells, and to defend these against dissolution, with a thick resinous cover, even in very acid moor waters.

ATMOSPHERIC HISTORY OF O_2 AND OF CO_2

One must distinguish between evidence as to the history of O_2 and of CO_2 in the atmosphere. The state of oxidation of ancient sediments belongs to the first category, the construction of shells might well belong to the second.

It is indeed, appropriate to consider both the history of atmospheric O_2 and CO_2 together. For if, as is postulated by modern theories, all oxygen at present is biogenic, there must have been, over billions of years, enough CO_2 to supply this oxygen through the medium of organic photosynthesis.

At present there is much more O_2 in atmosphere and hydrosphere than CO_2. The O_2, mainly contained in the atmosphere, is estimated at about $60 \cdot 10^{18}$ gmol, whereas the CO_2, mainly present in the hydrosphere, amounts only to some $3 \cdot 10^{18}$ gmol (ERICSSON, 1963; POSTMA, 1964). Consequently there must have been, in the past, a more or less continuous supply of CO_2. This is of course not difficult to visualize in relation to the outgassing of the earth, because CO_2 is the most common of volcanic gases.

Although nothing is known even of the present volume of volcanic CO_2 production, there is a border condition in these equations which does not contradict a possible origin of O_2 from CO_2. This is that fossil caustobioliths, resulting from photosynthesis, are estimated at $920 \cdot 10^{20}$ g C. This is equivalent to $2,700 \cdot 10^{18}$ gmol CO_2 (RUBEY, 1955). Compared with the present amount of oxygen, this seems to be ample, even when taking into account the loss of atmospheric oxygen to space.

THE OROGENETIC CYCLE IN THE EARTH'S HISTORY

If we want to follow the history of both O_2 and CO_2 there is one major geologic concept to introduce: that of the orogenic cycle. Major orogenies, or mountain-building periods, are found to occupy relatively short periods, of the order of $50 \cdot 10^6$ years, and to be separated from each other by much longer, relatively calm periods, of the order of several hundred times 10^6 years in duration. Each of the latter periods, called geosynclinal, together with the following orogenic period, forms one orogenic cycle.

During major orogenies both crustal movements and volcanic activity are at its maximum. It follows that on the one hand more material from deeper crustal levels will be brought to the earth's surface during orogenies than during geosynclinal periods. As most of this material is not fully oxidized, this implies a more active oxidation of surface minerals, and hence a depletion of atmospheric O_2 during orogenies. The stronger volcanic activity will, on the other hand, produce more CO_2 during orogenies, than during the quieter geosynclinal periods.

It also follows that during major orogenies the O_2 level will tend to fall, whilst the CO_2 level will tend to rise.

THE HISTORY OF OXYGEN AND CARBON DIOXIDE IN THE EARTH'S ATMOSPHERE

We may now turn to a graphic representation of the history of O_2 and CO_2 in the earth's atmosphere, as represented in Fig.1. We have, however, to remember that this is a representation both highly schematic and hypothetical. It will be clear, moreover, that this representation draws heavily on the study of BERKNER and MARSHALL (1965).

The diagram starts with the oldest rocks known at present, at $4.5 \cdot 10^9$ years ago (STUBBS, 1965). Major orogenies are represented, as given by PRIEM (1963).

Turning our attention in the first place to the history of atmospheric O_2, it is postulated that in the beginning, production of O_2 through inorganic photo-dissociation of H_2O was able to offset contemporaneous O_2 losses through oxidation of surface minerals. The atmospheric oxygen level was consequently maintained at the upper limit at which photodissociation of water takes place, that is at 35 cm equivalent path length (BERKNER and MARSHALL, 1965).

At about $3 \cdot 10^9$ years ago, life is thought to have developed the capability of organic photosynthesis, through dissociation of CO_2. Biogenic production of O_2 begins. Atmospheric O_2 level rises above the 35 cm equivalent path length, and, consequently, inorganic production of O_2 stops.

All things being equal, life is thought to expand exponentially, which is represented by straight lines of O_2 level rise. The slope of these lines is entirely hypothetical.

O_2 level must rise during quiet geosynclinal periods, and fall during major orogenies. During the latter periods, organic production of O_2 is thought not to be able to offset oxidation losses to the great volume of oxidable minerals brought to the earth's surface during these periods of lively crustal movements. There are, however, no data on the quantitative side of this rise and fall of the O_2 level.

At about $1.6 \cdot 10^9$ years ago oxygen level reached 0.01 PAL. Life spread to the oceans, and expanded strongly. There was a much greater production of O_2, but at the higher atmospheric level also a much stronger oxidation of surface minerals took place. This went on until about $1.2 \cdot 10^9$ years ago, when all surface materials were fully oxidized. The oxygen level during this period of transition is arbitrarily represented by a horizontal line.

The formation of eobionts and protolife through inorganic photosynthesis stopped at the beginning of this period of transition, or even some time before,

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Fig.1. Outline of the history of atmospheric O_2 and CO_2.

  a–p: Steps in the history of O_2, *1–19*: Same for CO_2.

  a–b: Inorganic photochemical production of O_2 through dissociation of H_2O, offset by oxidation of surface minerals, maintained at upper level of 35 cm equivalent path length.

  b: Start of organic photosynthesis.

  b–c, d–e, f–g, h–i, j–k, l–m: Organic production of O_2 exceeds depletion through oxidation of surface minerals during tectonically quiet periods. Straight slope of O_2 rise indicates exponentially expanding volume of life.

  c–d, etc.: Depletion of O_2 through oxidation of surface minerals exceeds organic production during major orogenies. But the amount of depletion decreases with time, as volume of life increases.

  i: O_2 level reaches 0.01 PAL. Life spreads to the oceans, stronger O_2 production, offset by stronger mineral oxidation. Beginning of the transition period from the an-oxygenic to the oxygenic atmosphere.

  j: Surface minerals oxidized, O_2 level rises further.

  m: Somewhere at this time respiratory animals develop. Slope of net O_2 production flattens.

  n: O_2 level reaches 0.1 PAL. Life spreads to the land. First major continental flora. Dated at Ordovician.

  o: O_2 level temporarily overshoots PAL, due to exuberance of continental flora. Dated at Upper Carboniferous.

  o–P(resent): O_2 level oscillates around PAL.

  1: Early CO_2 level, postulated to be higher than present, is arbitrarily indicated at 10 PAL.

  1–2, 3–4, 5–6, etc.: Depletion of CO_2 exceeds volcanic production during tectonically quiet periods. Compare *b–c*, etc. Slope steepening with time indicates stronger CO_2 depletion through the expansion of life; volcanic production supposed to be constant. This steepening is accentuated from point *7*, due to spreading of life to the oceans. Compare point *j*.

  2–3, 4–5, 6–7, etc.: Volcanic production of CO_2 exceeds organic depletion during major orogenies. Compare *c–d*, etc.

  12: Slope of CO_2 depletion flattens, due to the development of respiratory animals. Compare *m*.

  19: CO_2 depletion below PAL leads to alkalinity of ocean waters. Animals acquire shells. Dated at the beginning of the Cambrian.

  15–P(resent): Slope of CO_2 level depletion and accretion flattens, because balance of O_2 and CO_2 levels is now also influenced by organic feedback. Relative importance of volcanic production of CO_2 diminishes, as volume of life increases further.

when the rising O_2 level shielded the earth's surface from the shorter ultraviolet sunlight capable of these reactions.

Somewhere between $1 \cdot 10^9$ years and $0.6 \cdot 10^9$ years ago, animal life developed. Respiration diminished the slope of further rise in O_2 level, due to vegetative photosynthesis. Of course, plants do breathe also, but in plants capable of photosynthesis there is always a net production of O_2 over CO_2.

The slope of the rise of the O_2 level steepened again, however, at about $0.5 \cdot 10^9$ years ago, when during the Ordovician Period, vegetable life spread to the land, at the attainment of 0.1 PAL O_2.

O_2 concentration then overshot the present level during the Upper Carboniferous, was depleted again during the ensuing Hercynian orogeny, and has since oscillated around PAL.

Turning now to the history of the CO_2 level, it is seen that this is arbitrarily
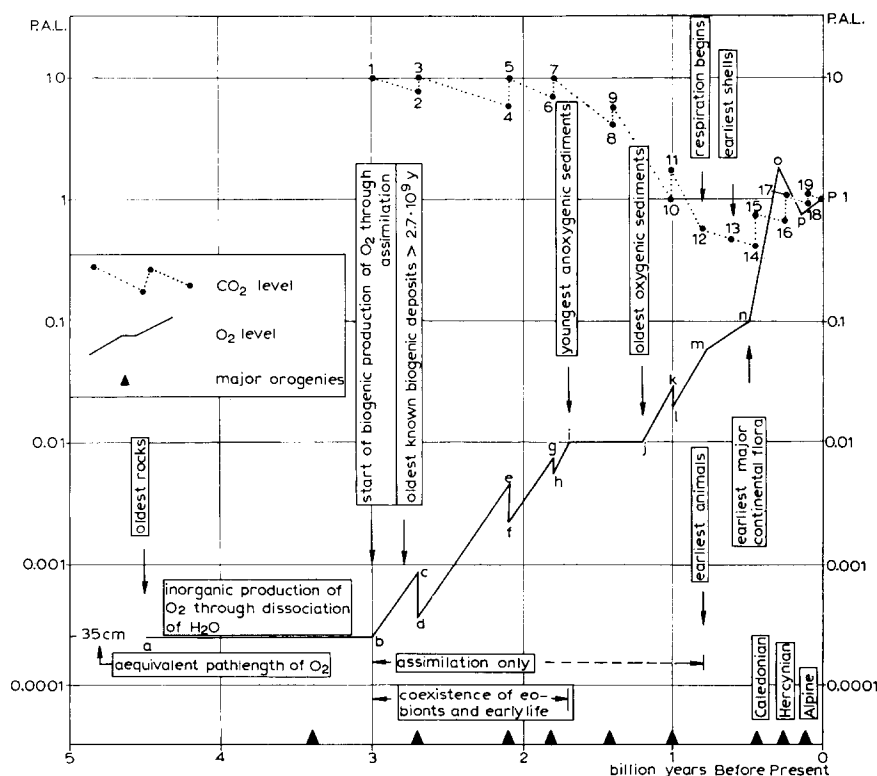

Fig.1. (Legend see p.54).

postulated at 10 PAL during early atmospheric history. The reason being that it is more comfortable to have more CO_2 at hand for organic photodissociation, than the relatively small amount available at present. There is a possible geologic corollary in the large amounts of carbonate biogenic deposits from Algae formed during the Precambrian, which points to a higher CO_2 level. Geochemical considerations, amongst others on the stability fields of iron minerals, seem to exclude the possibility of much higher values. L. G. Sillén, during the C.A.C.R. Symposium on atmospheric history, held at Visby in 1965, even thought 10 PAL a high value.

CO_2 level is depleted during the quiet periods of each orogenetic cycle, when losses due to organic photodissociation are not fully compensated by supplementation from volcanic activity. It rises again during major orogenies, due to stronger volcanism.

The slope of CO_2 level depletion during the geosynclinal periods must steepen with time, due to the expanding volume of vegetative life. It flattens, however, from the time of origin of animals, due to CO_2 production through respiration. As in the graph representing atmospheric O_2 history, there are no data on the quantitative amount of this fall and rise of the CO_2 level.

About $0.6 \cdot 10^9$ years ago, CO_2 depletion lead to a level below PAL, resulting in alkaline marine conditions. Marine animals learnt to construct shells, which set the stage for the "explosion of fossils" at the beginning of the Cambrian.

This might possibly also be related to the much debated late Precambrian Ice Age (HARLAND and RUDWICK, 1964). But here we enter the more normal geologic controversies, as mentioned in the introduction.

From that time, until present conditions were reached, CO_2 level is thought to have oscillated around PAL, inversely to the O_2 level.

The variations in CO_2 level are, from that date, damped by organic feedback mechanisms, involving expansion or reduction of the total volume of photosynthesis and respiration at higher or lower CO_2 levels.

CONCLUDING REMARKS

This completes a very concise representation of the history of atmospheric O_2 and CO_2. The author should like to draw attention at this stage to the words of caution given in the introduction, and repeat that this representation is highly schematic and hypothetical. Its main purpose is to illustrate possible effects from a number of processes which must have been active during the history of our atmosphere.

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