

Bulletin de la Société belge de Géologie Bulletin van de Belgische Vereniging voor Geologie	T. 95 V. 95	fasc. 2 & 3 delen 2 & 3	pp. 199-201 blz. 199-201	Bruxelles 1986 Brussel 1986
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LOWER CAMBRIAN EVAPORITES AND ATMOSPHERIC OXYGEN

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ABSTRACT. - The Lower Cambrian abundance of evaporites, especially of SO_4 salts and of continental red beds suggests a high level of atmospheric O_2 . This is discussed in the light of the opposite Ordovician-Silurian conditions : rare evaporites, widespread euxinic deposits. An evolutionary model with a fluctuating O_2/CO_2 ratio is proposed.

RESUME. - L'abondance des évaporites du Cambrien inférieur, notamment des sels en SO_4 , ainsi que des dépôts continentaux rouges, suggère que l'atmosphère était riche en O_2 . Cette relation est discutée à la lumière des conditions opposées régnant à l'Ordovicien-Silurien : évaporites rares, dépôts euxiniques étendus. Un modèle évolutif impliquant des fluctuations du rapport O_2/CO_2 dues à des réactions entre volcanisme et photosynthèse est proposé.

As emphasized by ZHARKOV (1981) evaporites deposits were particularly abundant during the Early Cambrian. As during the Late Silurian-Devonian and Permo-Triassic periods, these extensive evaporite deposits were associated and preceded (i.e. in the latest Precambrian) with widespread continental or epi-continental red detrital formations : purple sandstones and conglomerates in western Europe (Britain, Normandy and Brittany, Spain ...), "séries lie-de-vin" in Morocco, Zaigun shales and Lalun sandstones in Iran and neighbouring areas, Tommotian red marls in Siberia, red formations of the Upper Sinian in China and similar deposits in northern India and at the top of the Adelaïde series in Australia, etc... The distribution of these formations exceeds, therefore, that of normal climatic zones, as is the case for the Permian and Triassic systems which, besides the vast extension of New Red Sandstones in the northern hemisphere, comprise similar deposits in, for instance, the Beaufort and Red Beds Formations of

southern Africa.

The abundance of ferric oxide in these deposits as well as the important role played by the radical SO_4^{-2} suggests that the Eocambrian atmosphere was already rich in O_2 . Considering that there exists no actualistic reference for such extensive and thick red continental deposits, it is even possible that the proportion of O_2 in the air may have been then somewhat greater than what it is to-day (less than 21 %), owing to a smaller global amount of N_2 (about 78 % of the present day air), this gas being supplied slowly but regularly by volcanism, without being absorbed in any significant quantities by the crust. Correlatively, the Late Precambrian-Early Cambrian atmosphere must have been depleted in CO_2 , the presence of which would have facilitated the evacuation of iron from continents in the form of relatively soluble ferrous compounds.

The high proportion of oxygen must have stimulated the development of

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Metazoa while the depletion in CO_2 enabled them to extract CaCO_3 for their shells out of the soluble $\text{Ca}(\text{HCO}_3)_2$ contained in sea water, this molecule becoming unstable when there is a deficiency in CO_2 .

The problems raised by the assumption of an early enrichment of the air in O_2 are discussed below. Let us see first what could be its relation with a widespread and active sedimentation of evaporites, especially as a similar association with red beds is observed during the Devonian and Permo-Triassic periods. The first requisite is of course the existence of vast shallow lagoonal basins, practically at sea level. This may have been ensured by different but converging processes, all related with orogeny: a long peneplanation following a mountain-building period (as was the case after the Caledonian and Hercynian orogenies), i. e. the Late Precambrian phases such as the Baikalian, Cadomian, Panafrican ones; a slight relative rise of the sea level resulting from a total disappearance of the ice-caps that accompanied the preceding orogeny (a relation discussed below) and by continental-size tilt movements that represented either a final relaxation or the first signs of the next tectonic crisis: such were the Early Cambrian, Middle Devonian, Zechstein and Muschelkalk transgressions. The next requisite is that large continental areas are permanently exposed to sunny and dry weather, no fresh water being supplied by rivers to the inland lagoons. Inasmuch as arid land deposits were then more widely distributed than are desertic and sub-desertic belts to-day, this widespread aridity must have been determined by the composition of the atmosphere and may be accounted for by the conditions mentioned above: a relatively thin atmosphere owing to the small amount of N_2 would allow an intense solar radiation to reach the Earth's surface and this during a longer time per day than at present while the low atmospheric pressure would facilitate evaporation. At night, the same factors, especially the low partial pressure of CO_2 and the lack of any hot-house effects would allow an intense radiation of heat from the Earth, a rapid cooling of continents including areas occupied by shallow water while oceanic areas remained relatively warmer. This determined a flow of cold air from continents to oceans, thus sweeping away the vapour produced by the super-heated lagoons in day-time.

The notion of a high O_2 and low CO_2 content of the Early Cambrian atmosphere differs from the conclusions implied by all models based on the assumption of a continuous evolution of the atmosphere, especially of a continuous increase of its content in O_2 due to a photosynthesis and the development of plant life. The growth of the proportion of O_2 has been represented by a curve of exponential type (e. g. BERKNER & MARSHALL, 1964; SCHIDLÓWSKI, 1971, 1978) that remains fairly flat during the whole of the Precambrian and starts rising sharply towards the beginning of the Phanerozoic Eon, the Present Atmospheric Level (PAL) being reached towards the middle or the end of the Paleozoic. For CLOUD (1983), the O_2 level was about 10 % of the PAL at the time of

the apparition of the first shelly Invertebrates. HOLLAND (1984) envisaged very tentatively proportions around 0,2 of the PAL at the beginning of the Phanerozoic. He notes, however, a recent tendency to assume that notable proportions of O_2 had appeared much earlier in the Precambrian than was supposed on the base of previous models, but he holds for not tenable the extreme position of those (quoting DIMROTH & KIMBERLY, 1976) who come back to a uniformitarian conception of the atmosphere, including that of the Early Precambrian.

In the author's view, the assumption that the Early Cambrian atmosphere was rich in O_2 and poor in CO_2 - as suggested by large scale geological data - is incompatible with the continuous and exponential evolutionary model as well as with the more or less uniformitarian one, but it becomes perfectly receivable in the frame of a fluctuating and more or less cyclic evolution of the atmosphere (BRUNN, 1983). The theoretical considerations that lead to admit such fluctuations are the following:

- a. the small thickness and weight of the atmosphere, its direct exposure to the influence of volcanism, of solar radiations and biological processes;
- b. the discontinuous evolution of the Earth's crust which underwent repeated orogenic and volcanic crisis, well known in the Phanerozoic, more numerous in the Precambrian for which they are largely used as stratigraphic limits;
- c. feed-back reactions between volcanism supplying CO_2 and plants liberating free oxygen.

The enrichment of the Late Precambrian and Early Cambrian atmosphere in O_2 appears thence as a direct consequence of the world-wide proliferation of Cyanobacteria (Blue Algae) as shown by the widespread occurrence of thick stromatolitic carbonates shortly before the expansion of red detrital formations and sometimes immediately underlying them (e. g. the "Calcaires inférieurs" in Morocco, the Soltanieh dolomites in Iran, Yudomian limestones in Siberia). Considering the great quantities of CO_2 that were fixed into the carbonates through a secondary consequence of the photosynthetic activity of Blue Algae (the primary one being the creation of organic matter by splitting CO_2 and H_2O , thus liberating oxygen), the CO_2 content of the atmosphere must have been high, following the Late Precambrian orogeny mentioned above. Blue Algae being adaptable and ubiquitous, these processes could go very far in cleaning the air of its CO_2 and enriching it in O_2 .

Things are clearer because better dated if instead of looking back, one looks ahead at the developments that followed the Early Cambrian. The Caledonian orogeny, accompanied by volcanism, gathered impetus towards the middle Cambrian. Evaporitic deposits underwent a sharp fall. Vegetation being still scarce, this pollution may have been the cause of the peculiar deposits known as "Alum shales". Perhaps was it not foreign to the disappearance of the Archeocyata which were vulnerable, being, like Corals,

totally open to their environment. But the real change occurred from the Tremadoc onwards, both for evaporites and for other types of sedimentation. The start was given by a powerful submarine ophiolitic magmatism and it was followed by the Ordovician mainly calcalkaline and gas-rich volcanism that accumulated thousands of meters of volcano-clastic material all along the Caledonian-Appalachian, Euro-Asiatic and Pacific ranges. Enormous quantities of CO₂, SO₂ and other potentially acid constituents were thrown into the atmosphere. The world-wide invasion of graptolitic black shales reveals that anoxic conditions of sedimentation were easily obtained. It primarily marks the appearance of a new and swarming vegetation, at first algal, then terrestrial (but primitive and non-ligneous) as indicated by the relatively fine grain of the Silurian dark flysch deposits. This renewal may have been due to mutations prompted by volcanic disturbances of the ozone layer but the vegetation must have been thereafter stimulated by the abundance of CO₂ in the air.

The volume of the evaporites was, according to ZHARKOV, smaller by two orders of magnitude during the Ordovician than during the Early Cambrian. This reduction may be understood in the light of what is known to-day of the hot-house effect due to a high percentage of CO₂ in the air and by opposition to the situation during the Early Cambrian described above. The hot-house effect stifled the contrast between continental and oceanic temperatures and atmospheric pressures. This caused a stagnation of vapor over continental areas, a widespread and more or less constant nebulosity that increased the hot-house effect, regular precipitations that again favoured vegetation. A similar uniformity prevailed during the Upper Carboniferous as shown by the absence of seasonal rings. Such conditions obviously hindered the formation of evaporites, except in particularly propitious situations of latitude and exposition. They were also unsuitable for the accumulation of continental red beds, especially as iron tended to be washed down to the sea by acid rains as Fe²⁺ compounds, accompanied by sulfur. In polar regions, regular snowfalls accumulated ice-caps.

At length, the burial of organic matter purified the air of its CO₂ and enriched it in O₂, as Blue Algae had done in their time, so that continental or epi-continental red beds reappeared in the Late Silurian to attain their full development together with evaporitic basins in the Old Red Sandstones. Concomitantly, the new animal forms that had come into being owing to the mutations of the Ordovician period, at least those that survived to the poor atmospheric conditions, entered a phase of vigorous expansion and diversification, especially Vertebrates and Corals, both groups having high requirements in oxygen.

Glancing back at the Precambrian, important evaporitic basins are reported only from the Late Proterozoic (Amadeus and Officer basins of Australia). Further back in time, HOLLAND (1984) mentions the Mac Arthur Marble that is

thought to represent a replacement of sulfates and is 1.8 to 1.4 Ba old. This is also the time of the first important continental red beds and of the appearance of Eucaryotes, both indicating the presence of atmospheric oxygen. Stromatolitic carbonates started also to be thick and widespread. More precise stratigraphic data may bring to light some relations between successive phases of volcanism, of stromatolitic limestones and of red beds during the 1.2 Ba of the Proterozoic.

Further back still, during the Archean, only casts of evaporitic minerals have been found. It may be pointed out that, if the Early Archean atmosphere was deprived of oxygen, there is a problem concerning the association of Ca and S. Could it have taken the form of oldhamite (CaS) that is found on meteorites? This is only a question. On the whole, this paper was intended to emphasize the importance of the atmosphere as a sensitive and reactive medium ensuring the link between phenomena and processes taking place under and above the Earth's surface.

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