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The late Paleozoic oxygen pulse and accumulations of petroleum source rocks and coal

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Abstract: Recent geophysical and geochemical data and theoretical modeling indicate high levels of atmospheric O_2 (up to 35 %) during the Carboniferous-Permian. I suggest that this O_2 pulse had a substantial impact on global accumulations of petroleum source rocks and coal during this geological period.

Keywords: oxygen, petroleum source rocks, coal, Carboniferous-Permian.

INTRODUCTION

Recent geophysical and geochemical data, as well as theoretical models suggest that the Paleozoic/Mesozoic periods (65 Ma – 570 Ma) was marked by significant changes in the atmospheric chemistry.[1] These data and models indicate that atmospheric O_2 increased from approximately 18 % to 21 % between the middle and late Devonian (*ca*. 380–360 Ma) and then rose sharply to about 35 % by the late Carboniferous-early Permian (*ca*. 290 Ma), a remarkable value compared with the present atmospheric level (PAL) of 21 % (Fig. 1). Throughout the middle/late Permian (290–250 Ma), atmospheric O_2 steadily declined and dropped to about 15 % by the end of the Paleozoic (250 Ma). These O_2 fluctuations are believed to have been largely caused by biotic/abiotic factors and had dramatic geological, geochemical and biological consequences. I focus here on the substantial changes (over a relatively short period of geologic time) of the global accumulations of petroleum source rocks and coal during the Carboniferous-Permian. I argue that this change was driven by an increased global O_2 supply during this geological interval.

PETROLEUM SOURCE ROCKS

Modern organic geochemistry indicates that most of petroleum source-rocks are organic-rich ancient sedimentary rocks of marine origin containing mainly

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type II kerogen, which was sufficiently rich in hydrogen to generate petroleum during thermal maturation (catagenesis).[2] This source kerogen originated from marine humic substances during diagenesis. The principal source of these humics was the organic detritus of single-celled phytoplankton which lived in the upper layers (up to *ca*. 200 m in depth: euphotic zone) of seawater.

Petroleum source rocks of marine origin were deposited under anoxic conditions. Preservation of marine humic matter (the kerogen precursor) is a crucial point for the deposition of petroleum source rocks. In general, the combination of high bioorganic productivity (phytoplankton) in the surface seawaters and depleted O_2 in the seawater column generated conditions favorable to enhance the preservation of (phytoplanktonic) humic matter in the underlying sediments. The most critical factor affecting the preservation (or destruction) of these humics in a marine sedimentary milieu was the concentration of O_2. Indeed, most of the oxidation occurring in the seawater column and sediments was biological, and these biological processes required O_2. The concentration of O_2 in the seawater column and sediment was, therefore, the limiting factor (*i.e.*, anoxic deposition of source rocks could occur where the seawater/sediment interface laid within the O_2 depleted zone).

O_2 was mainly supplied to seawater by downward movement of O_2-rich water from the O_2-saturated surface seawater which was enriched by O_2 mainly through exchange with the atmospheric O_2. Thus, an increased global atmospheric O_2 supply (and its atmospheric partial pressure) would have enhanced the O_2 level in the surface seawater, including a deepening of the oxic/anoxic interface, a greater O_2 penetration into the sediments, an increase O_2 exposure time of the accumulating bioorganic remains and a decrease of the sulfide level, which is essential for an anoxic sedimentary milieu. The consequence of the increased supply of O_2 into the surface seawater was a rise of O_2 in the seawater column and within the sediments on the seabed. In other words, the high atmospheric O_2 and increased oxygenation of the seawater would have disfavored the widespread occurrence of marine anoxia and associated deposition of petroleum source rocks during the Carboniferous-Permian.

The stratigraphic distribution of petroleum (as well as of gas and coals) and its source rocks in the world have been studied by organic geochemists and petroleum geologists for decades.[3–9] The available geochemical evidence indicates that the source rocks present in the stratigraphic record are unevently distributed in geological time. Figure 1a shows the time distribution of the relative areal extent of petroleum source rocks, expressed as a percentage of the total source rock area, of the Paleozoic/Mesozoic periods. According to Klemme and Ulmishek,[9] major periods for the widespread formation and preservation of source rocks in the Paleozoic/Mesozoic eras include Silurian, late Devonian-early Carboniferous, late Carboniferous-early Permian, late Jurassic, and the middle Cretaceous (Fig. 1a). Indeed these five stratigraphic intervals contain more than 90 % of the source rocks

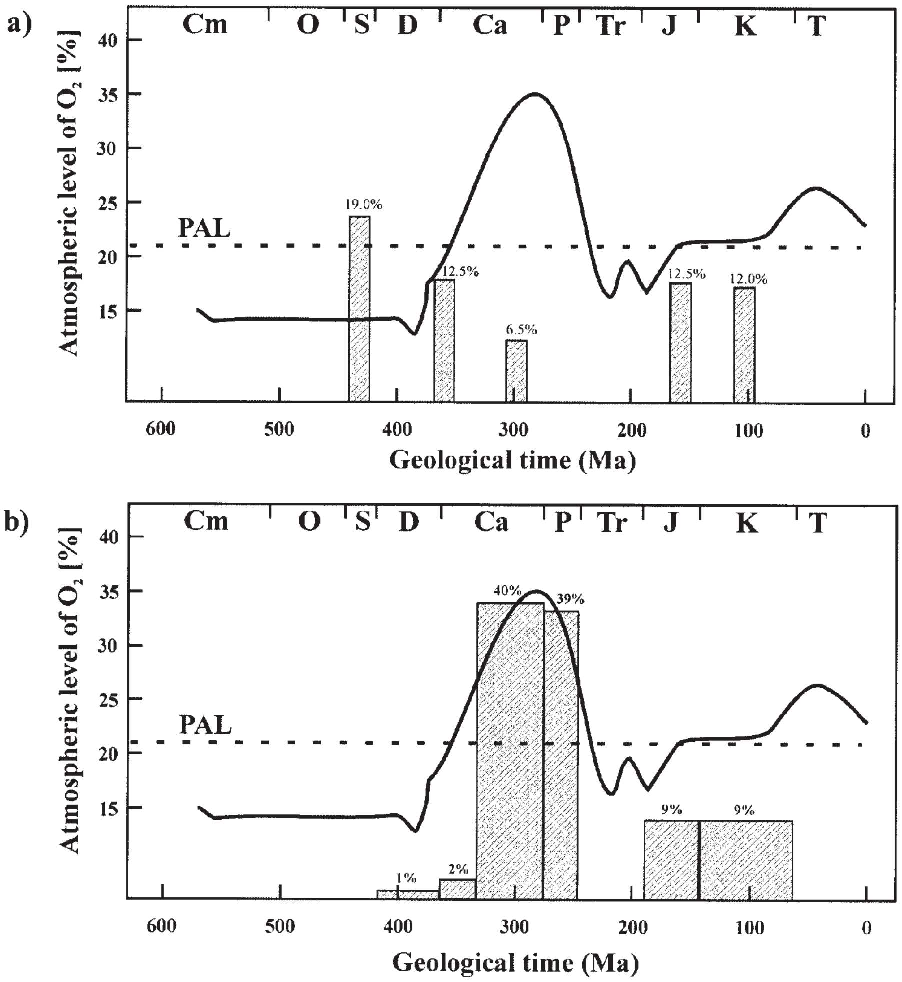

Fig. 1. (a) Relative areal extent of petroleum source rocks, given as a percentage of the total world's source rock area, of the Paleozoic/Mesozoic periods. Adapted from Klemme and Ulmishek,[9] Cm, Cambrian; O, Ordovician; S, Silurian; D, Devonian; Ca, Carboniferous; P, Permian; Tr, Triassic; J, Jurassic; K, Cretaceous; T, Tertiary. (b) Stratigraphic distribution of coal reserves, given as a percentage of the total coal reserves of the world. (Note the lack of coal deposits prior to the Devonian, when vascular plants evolved).

and generated approximately 80 % of current petroleum reserves of the world (ca. 1.4×10^{11} tones) in relatively small anoxic sedimentary basins. The source rock minimum of the Paleozoic/Mesozoic periods correlates fairly with the late Carboniferous-early Permian high (to 35 %) atmospheric O_2. This clearly demonstrates that it is likely that the Paleozoic O_2 pulse had a substantial impact on the global deposition of source rocks, although a diversity of other biotic/abiotic factors (including sea-level changes and reduced temperature) may also have contributed synergistically to this impact.

COAL

Coal is one of the most significant natural resources in the world, estimated in 1996 at around one thousand billion (1×10^{12}) tones of coal reserves. Approximately 65 % of the fossil fuels are coal.

At the present time, most investigators believe that coal was formed mostly from the altered aromatic biopolymer of terrestrial vascular plants-lignin, which was selectively preserved. Essentially all of the other major components of these plants, including the cellulose were lost through microbial and other diagenetic activities in anaerobic coal-forming peats deposited in paralic (*i.e.*, marginal marine) areas and deltaic swamps. An increased O_2 level of the atmosphere was advantageous for terrestrial vascular plants by enhancing their oxygen-dependent biosynthesis of lignin; these plants dominated during the late Paleozoic. Indeed, the Carboniferous-Permian vascular flora (ferns and primitive gymnosperms, as well as sphenopsids and lycopods) had increased height and arborescence, which would have been facilitated by a higher level of atmospheric O_2 and associated greater atmospheric density. Consequently, high O_2 concentrations in the atmosphere would have favored the global occurrence of terrestrial vascular plants. This, in turn, would have favored widespread accumulations of terrestrial humic matter (rich in lignin), which are responsible for the worldwide coal deposits. Hence, periods of high atmospheric O_2 level should be characterized by enhanced coal deposition.

Available evidence indicates that coal was also unequally distributed during the Paleozoic/Mesozoic. Figure 1b shows the distribution of coal (world reserves) as a function of geological age. Large coal deposits only started to be formed after the evolution of land plants in the Devonian period, some 400 million years ago. The most prolific coal production period is around the Carboniferous-Permian when the largest coal deposits (for all geologic time) were formed, which correlates well with the high O_2 at this time. This interval integrates approximately >80 % of the world coal reserves, but it amounts to *ca.* 17 % only of the time elapse since the Precambrian.

Holland,[10] Berner,[1,11] Berner and Canfield[12] rationalized that the marked increase of atmospheric O_2 during the late Carboniferous-early Permian was caused by the rise of vascular land plants and the consequential increased production of O_2 by the burial in sediments of terrestrial (lignin-rich) humics which were resistant to microbial decomposition. Berner[11] reported large increase in ^{13}C of the ocean and atmosphere at that time was due to an increased removal of ^{12}C from seawater and the atmosphere as organic matter buried in the sediment. Berner[1,11] explains this increase by the production of lignin which led to a greater burial of organic carbon (both in terrestrial peats and in the sea), enabling the formation of vast coal deposits during the Carboniferous-Permian. Robinson[13] proposed that high levels of atmospheric O_2 during the Carboniferous-Permo periods facilitated the development of fire resistant (vascular) plants.

И З В О Д

УТИЦАЈ ПУЛСА КИСЕОНИКА ИЗ КАСНОГ ПАЛЕОЗОИКА НА АКУМУЛАЦИЈУ НАФТНИХ ИЗВОРНИХ СТЕНА И УГЉА

ПАВЛЕ И. ПРЕМОВИЋ

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Скорашњи геофизички и геохемијски подаци и теоретско моделирање указују на висок ниво атмосферског O_2 (до 35 %) у току прелаза геолошких периода карбона и перма. Сматрам да је тај пулс O_2 имао значајан утицај на глобалну акумулацију нафтних изворних стена и угља у току овог геолошког раздобља.

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