IN SEARCH OF MOST ABUNDANT NATURAL GEOMOLECULE ON EARTH

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Abstract

Micromolecular evolution based on some microfossils is not an easy task for a paleontologist. In this paper the significance of a biomarker to study the ancient paleoenvironment is investigated which shows a strong co-relation between the source of the marker and availability of atmospheric oxygen. Such an important group of biomarker is Hopanoid, which is a large molecule containing five rings with an extended tail hanging off one end .They are unique to bacteria, but otherwise are quite widely distributed. However, hopanoids with some specific structural modifications have a much more limited distribution and biological specificity. Like 2-methylhopanes in the environment is a marker for cyanobacteria, and that is why when we find them in very old rocks, we can infer that cyanobacteria were alive and well at that time.

Key words

Hopanoid, bacteria, cyanobacteria, oxygenic photosynthesis, paleo-environmental marker

Introduction

Sometimes paleontologists used to investigate the signature of an ancient life on earth in a different way. Instead of depending on animal fossils, they used microchemical fossils. Molecular fossils are remnants of the actual lipid molecules that formed the cell membranes of ancient organisms. It is the organic remains that are preserved in the rocks. Certain lipids which are fat-like molecules that are mainly composed of carbon and hydrogen, are very resistant to degradation, and under the right geologic conditions those can be preserved in a recognizable form for billions of years. Many of these lipids consist of little more than straight hydrocarbon chains, which indicates sorts of creatures produced them. However, certain structurally complex lipids carry much more information, because their unique carbon skeletons can be recognized in ancient deposits and (in some cases) help us to know who produced them. We, generally call such structures as "molecular fossils", or biomarkers.

Different biomarkers were discovered till date. Amongst them the most abundant as well as natural product of earth is **Hopanoid Biomarker**. Most commonly, hopanoids are generally found in selective groups of aerobic bacteria. This has lead to a rather controversial conclusion that O_2 first accumulated in the earth's atmosphere well before the evolution of photosynthetic

cyanobacteria. Although there was no such obligate requirement for oxygen in their biosynthesis. Therefore, hopanoid synthesis might also be possible in anaerobes.

Review of Literature

Biomarkers are potentially useful because the three domains of extant life i.e. bacteria, archaea and eukarya have signature membrane lipids with recalcitrant carbon skeletons. These lipids turn into hydrocarbons in sediments and can be found wherever the record is sufficiently well preserved.It is often said that hopanoids are "the most abundant natural products on Earth" [1, 2]. Most commonly, hopanoids are found in selected groups of aerobic bacteria. [3]. The functional forms of hopanoids in bacteria are the amphiphilic bacterio hopane polyols(BHPs).

Hopanoids, including 2α-methylhopanes from photosynthetic bacteria (cyanobacteria), were discovered by Roger Summons and colleagues as molecular fossils preserved in 2.7 Gya shales from the Pilbara, Australia, which indicates that oxygenic photosynthesis evolved well before the atmosphere became oxygenated [4].Bacterial hopanoids and other polycyclic terpenoids were acted as membrane strengtheners, and may have done well so for at least 2.4-2.7 billion years. Bacterial modified hopanoids had been found in cyanobacteria, but other bacteria are now known to produce the same molecules under appropriate culture conditions [5].2-methylbacteriohopanepolyols occur in a high proportion of cultured cyanobacteria and cyanobacterial mats. Their 2α-methylhopane hydrocarbon derivatives are abundant in organic-rich sediments as old as 2,500 Myr.of Proterozoic period. These biomarkers may have helped to discover the age of the oldest cyanobacteria and the advent of oxygenic photosynthesis. They could also be used to in the ecological importance of cyanobacteria through geological time scale.

In fact, hopanoids were recognized as chemical fossils well before their bacterial origins were established. Methanotrophic bacteria and acetic acid bacteria biosynthesize a range of 3β-hopanoids [6]. The corresponding 3β-methylhopane hydrocarbons could be derived from either group of bacteria but a profound ^{13}C depletion that has been observed in several of their sedimentary occurrences points to methanotrophic sources being more important [7]. 2β-Methylhopanoids are produced by many cyanobacteria and have few other demonstrated sources and, accordingly, it is hypothesized that the corresponding sedimentary 2α-methylhopane hydrocarbons are biomarkers for cyanobacteria [8].

HOPANOID BIOMARKER

(POLYCYCLIC ISOPRENOIDS)

[Hopanoids are "the most abundant natural products on Earth"Review Presented in Tabular Form]

Biomarker	Taxa specification	References
C_{30}-hopanes	Mostly bacteria, few eukaryotic species (e.g. some cryptogams, ferns, mosses, lichens, filamentous fungi, protists)	Rohmer et al., 1984
C_{31} to C_{35}hopanes	Known for Bacteria.	Ourisson and Albrecht, 1992, Rohmer et al., 1984

C_{32} to C_{36} 2α-methylhopanes	Mostly cyanobacteria.	Bisseret et al., 1985, Summons et al., 1999
C_{32} to C_{36} 3β-methylhopanes	Diagnostic for cyanobacteria and prochlorophytes. 2.4 by aneoarchean period.	Zundel and Rohmer, 1985 Summons and Jahnke, 1992
28,30-dinorhopane, 25,28,30-trinorhopane (TNH)	Diagnostic for some micro aerophilic proteobacteria (certain methylotrophs, methanotrophs and acetic acid bacteria)	Grantham et al., 1980, Peters and Moldowan, 1993

Methodology

Here gas chromatography is the main technique, which was used to separate out the individual components of very complex mixtures. High resolution gas chromatography using fused silica capillary columns is the ideal method to obtain maximum separation of compounds over a wide range of molecular weights. Compounds must be volatile for this work to be done. Therefore, in the case of complex lipids found in soil and environmental samples, we must hydrolyze and derivatize (the same) in order to obtain the core components in volatile form. These lipid subunits include fatty acid methyl esters and trimethylsilyl ethers of sterols and hopanoids. We often work on petroleum samples, which are composed of many hundreds of thousand different compounds. Computerized Gas Chromatography – Mass Spectrometry (GCMS) is the principal method used to detect and identify compounds by exploiting the mass variations of different compounds. A typical GCMS system usually performs six functions such as: transfer of separated compounds to the ionizing chamber of the mass spectrometer, ionization, massanalysis, detection of the ions by the electron multiplier, acquisition, processing and display of data by computer and compound separation by gas chromatography.

A syringe injects a known amount of the saturated fraction dissolved in hexane into the GC column, which is a long, thin capillary tube(0.32 mm wide and 60 metres long). The inner surface of the column is coated with a film of nonvolatile liquid, called the stationary phase. The temperature of the column is gradually raised, using a temperature-programmed oven, causing the compounds to move. Each injected sample is vaporized and mixed with helium, an inert carrier gas, which is also called the mobile phase.

The larger molecules are retained by the stationary phase at the head of the column, a process called ‘cold trapping’. The mobile phase and sample mixture move along the column, while components are separated as they are repeatedly retained by the stationary phase and released into the mobile phase depending on their volatility and affinity for each phase. The compounds elute, or are washed out from the end of the column, at different rates and are analyzed by the mass spectrometer.

Limitations

One of the major problems with 2-methylhopanes and indeed with most biomarkers is that it is very hard to tell how many different organisms have the ability to make that particular compound. It was observed that a couple of species outside the cyanobacteria makes 2-

methylhopanes, though there are still tons of thousands of organisms that have not been specifically tested for this ability. They are common elements of sedimentary rocks formed as early as 1.64 billion years ago and are estimated to have a greater mass than all other natural products from living organisms combined.

As the number of sequenced bacteria and the availability of genetic approaches have expanded, it has become clear that remarkably diverse organisms produce hopanoids. It is therefore, difficult to attribute hopanes in the rock record at the advent of a specific phylogenetic group, metabolic process or environmental context. Lack of proper samples sometimes is another problem for this type of investigation. Sometimes it's difficult to locate proper source of material distinctly for a particular biomarker and sometimes it's difficult to mark a particular organic molecule for a specific taxa.

Conclusion:

Therefore, from the above mentioned discussions and results it can be said that Methylated hopanoids i.e. the 2-methylhopanepolyols, are believed to be the products exclusively of the cyanobacteria, and 2α-methylhopanesin ancient sedimentary rocks were, thus, interpreted to be indicators for oxygenic photosynthesis .

Oxygenic photosynthesis is widely accepted as the most important bio-energetic process happening in earth's surface environment. It is thought to have evolved within the cyanobacterial period, but it has been difficult to determine when it was being started. Evidence based on the occurrence and appearance of stromatolites and microfossils which indicates that phototrophy occurred as long ago as 3,465 MY although no definite physiological inferences can be made from these objects.The rise of atmospheric oxygen has driven environmental changes and biological evolution throughout much of earth's history and was enabled by the evolution of oxygenic photosynthesis in the cyanobacteria.

References:

1.Brocks, J.J., and Summons, R.E., 2004, "Sedimentary Hydrocarbons, Biomarkers for Early Life",In: Treatise on Geochemistry., Vol 8,Biogeochemistry.Schlesinger WH (ed)., Elsevier-Pergamon, Oxford, pp. 63-115

2.Buick, R., 1992 "The antiquity of oxygenic photosynthesis:evidence from stromatolites in sulphate-deficient Archaeanlakes". Science 255, 74–77.Retrieved May 14,2019 ,from https://science.sciencemag.org/content/255/5040/74.

3.Innes ,E.Helen ,Bishop, N. Andrew ,Head,M. lan,Farrimond,Paul.,1997,"Preservation and diagenesis of hopanoids in Recent lacustrine sediments of Priest Pot, England".In Organic Geochemistry 26(9).pp.565-576 ·Retrieved May 14, 2019

from, https://www.sciencedirect.com/science/article/pii/S014663809700017X.

4.Zundel,M., and Rohmer,M., 1985“ Prokaryotic triterpenoids. l. 3??-Methylhopanoids from Acetobacter species and Methylococcus capsulatus”. In European Journal of Biochemistry 150(1).pp.23-7.Retrieved April14,2019from,https://www.researchgate.net/publication/19234434_Prokaryotic_triterpenoids_I_3-Methylhopanoids_from_Acetobacter_species_and_Methylococcus_capsulatus.

5.Summons,R.E.,Jahnke, L.L.,Hope, J.M., Logan, G.A.,1999 “2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis”. In Nature 400(6744).pp. 554-557.Retrieved May 10,2019 https://www.ncbi.nlm.nih.gov/pubmed/10448856.

6.Bisseret,P.,Zundel,M.,Rohmer,M.,1985“Prokaryotic triterpenoids2. 2β-Methylhopanoids from Methylobacterium organophilum and Nostoc muscorum, a new series of prokaryotic triterpenoids.”inEur. J. Biochem. 150(1), pp.29-34.

RetrievedMay20,2019fromhttps://febs.onlinelibrary.wiley.com/doi/full/10.1111/j.1432-1033.1985.tb08982.x

7.Brocks, J.J., Logan ,G.A., Buick, R., and Summons, R.E., 1999, “Archean molecular fossils and the early rise of eukaryotes”, in Science285(5430),pp. 1033–1036. Retrieved June 06, 2019 from https://science.sciencemag.org/content/285/5430/1033.long.

8.Blankenship, R. E. & Hartman, H. 1998,“The origin and evolution of oxygenic photosynthesis.”in Trends in Biochem. Sci. 23(3), pp.94-97.Retrieved June 06, 2019from https://www.cell.com/trends/biochemical-sciences/fulltext/S0968-0004(98)01186 4?_returnURL=https%3A%2F%2Flinkinghub.elsevier.com%2Fretrieve%2Fpii%2FS096800049 8011864%3Fshowall%3Dtrue.