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Bacteriohopanepolyol lipids reveal past biogeochemical processes

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Global biogeochemical cycles such as the carbon and nitrogen cycles are regulated by microorganisms. Phytoplankton fix carbon dioxide and methanotrophic bacteria oxidise methane to carbon dioxide; ammonia oxidising microbes convert ammonia to nitrites, and anaerobic ammonium oxidising (anammox) bacteria transform ammoniums and nitrites to dinitrogen. Past fluctuations in microbial processing inform more accurate future modelling of the effects of climate change.

As bacteria rarely leave fossils, lipid biomarkers such as bacteriohopanepolyols (BHPs) are used to identify their past presence in sedimentary records. BHPs have been used to elucidate the occurrence of marine anammox and peatland methanotrophy (oxidation of methane to carbon dioxide) millions of years ago.

Studying biogeochemical cycles

In the Anthropocene, human activity is drastically changing biogeochemical cycles. Stored carbon is burnt for energy, releasing carbon dioxide, and global nitrogen fixation (the transformation of nonreactive nitrogen gas to reactive nitrogen species such as ammonia) is dominated by the Haber-Bosch process. However, such changes are not unprecedented in geological time. For example, Jurassic and Cretaceous hot-house climates are analogous to today's increased fluxes in greenhouse gases. During these periods, ocean anoxia was widespread, colloquially known as ocean "dead zones", where multicellular life was unable to survive. In order to develop accurate models, therefore, we must go "back to the future" – investigating geological samples.

Studying microbes in ancient biogeochemical cycles presents unique challenges as they do not leave hard-bodied fossils. Whilst there have been considerable improvements in the field of ancient DNA analysis, they have only been applied to samples a few million years old (*1*). In contrast, microbial lipids are preserved for at least 700 million years (*2*), making lipid

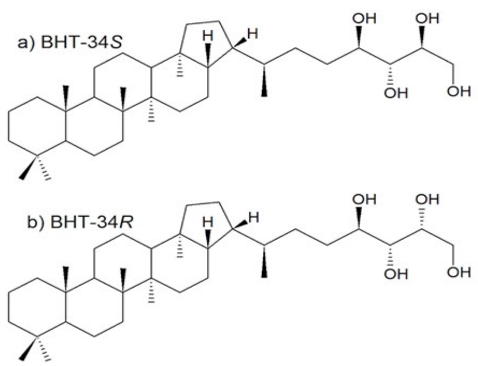

Figure 1. Diastereomers of bacteriohopanetetrol (BHT) include a) BHT-34S and b) BHT-34R.

biomarkers ideally suited to investigate microbial drivers of past carbon and nitrogen cycles.

Bacteriohopanepolyol lipids

BHPs are membrane lipids found in approximately 10% of bacteria, composed of a multi-ring hopane backbone and a functionalised sidechain (**Figure 1**). BHPs have an analogous function to sterols in eukaryotes: they allow bacteria to maintain membrane fluidity during stressful conditions (e.g. extreme temperature) (*3*). While some BHPs, such as bacteriohopanetetrol (BHT-34*S*; **Figure 1a**), are ubiquitous in the environment, others are produced by a limited set of bacteria, making them biomarkers for those species and their environments. For example, two diastereomers of BHT-34*S*, BHT-34*R* (**Figure 1b**) and BHT-*x* are linked to specific bacterial producers which include anammox bacteria and methanotrophs (*4*).

Marine anammox BHPs

Microorganisms drive redox changes in the nitrogen cycle and, before the introduction of the Haber-Bosch process in the early 20th century, were responsible for nearly all nitrogen fixation on Earth. Conversely, microbial activity can also decrease the availability of reactive nitrogen via two anaerobic processes: denitrification and anaerobic ammonium oxidation. *Ca. Scalindua* is the only marine anammox genus and removes ~ 30% of reactive nitrogen, a limiting nutrient to phytoplankton, from the modern ocean (*5, 6*). In the Mediterranean, orbital cycling influences the hydrological cycle, causing periodic eutrophication every 21,000 years. These events appear in sedimentary records as sapropel events. Anammox bacteria produce unique ladderane lipids (**Figure 2**) and they can be traced using the abundance of ladderane lipids in sapropel sediments up to ~125,000 years old (*7*). However, due to their highly strained cyclobutane rings, ladderane lipids do not persist beyond this time (*7*). *Ca. Scalindua* are the only known producer of BHT-*x* (*4*), making it an additional biomarker for marine anammox. BHT-*x* was found in a 2.67 million-year old sapropel sediment, highlighting the role of anammox in Pliocene Mediterranean sapropels (*7*).

Anammox bacteria are also involved in deep ocean carbon fixation, converting inorganic carbon to organic biomass. Recent study of the isotopic signature of BHT-*x* in the Arabian Sea dead zone found that anammox bacteria biomass composed ~ 20% of the organic matter deposited to the sediment (*8*). Anthropogenic climate change and agricultural intensification are projected to enlarge ocean dead zones, with potentially devastating impacts on marine ecology. Anammox bacteria may slow the rate of carbon dioxide increase through carbon fixation and sequestration in dead zones.

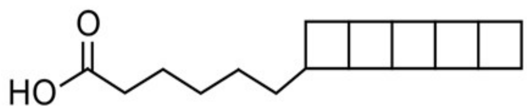

Figure 2 . C_{18}-[5]-ladderane fatty acid structure (7).

Peatland methanotroph BHPs

Peatlands play a key role in the carbon cycle, as they sequester ~ 25% of the world's carbon (*9*). They are also the largest natural source of atmospheric methane, produced by methanogen microbes in anoxic settings. Methane is a potent greenhouse gas: it has over 25 times the global warming potential of carbon dioxide. Methanotrophic bacteria consume methane, reducing emissions. However, climate modellers must understand the effects of environmental changes on methanotrophs. Many terrestrial species produce aminoBHPs such as aminotriol and aminotetrol (**Figure 3**), which are used to distinguish them (*10*). *M. palustris* is an acidic peatland methanotroph proxy, also producing BHT-34*R* (*4*). Abundant aminoBHPs in a well-preserved 56 million-year old peat core, the Cobham Lignite (UK), indicate substantial peatland methanotrophy occurred during this period (*11*). The higher abundance of these methanotroph-derived aminoBHPs in the Cobham Lignite core compared to modern peats may suggest an intensification of methane production and consumption during the Paleocene–Eocene Thermal Maximum, an abrupt global warming event in Earth history (*11*).

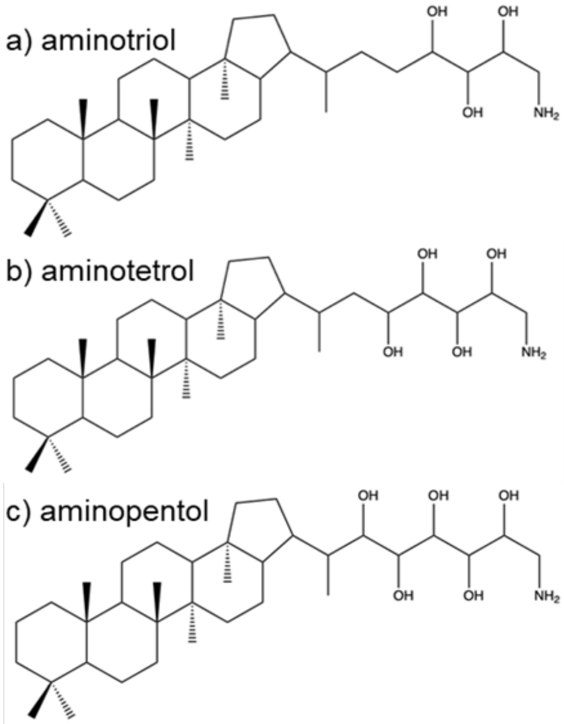

Figure 3. Structures of a) aminotriol, b) aminotetrol and c) aminopentol.

Conclusion

BHP biomarkers have the power to reveal the microbial processes underlying biogeochemical cycles, both in modern times and through geological history, aiding in modelling the present and the future.

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