IAPETUS

NERC DOCTORAL TRAINING

On-line position specific stable isotope analysis of diploptene, a molecular proxy for methanotrophy

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University of Glasgow, School of Engineering

In partnership with: University of Glasgow, Geographical and Earth Sciences and Newcastle University, Civil Engineering & Geosciences

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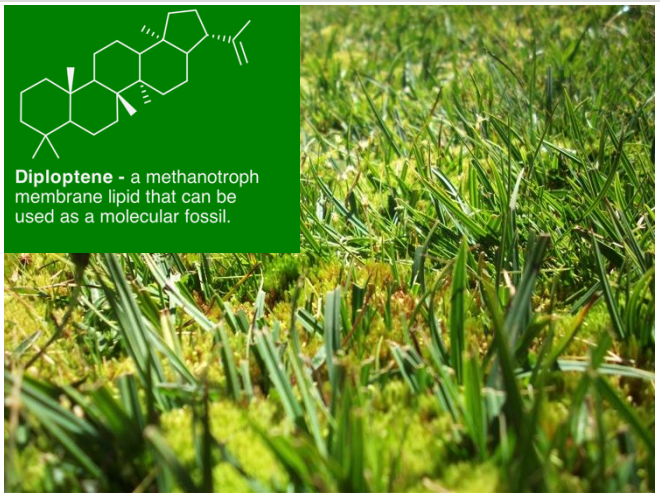
Key Words	**Methane, Position Specific Stable Isotope Analysis, Molecular Fossils, Peatlands Dynamics, Organic Geochemistry**

Overview

Methane (CH_4) is a greenhouse gas that is 25-times more potent than CO_2 at trapping heat at the Earth's surface. Methane emissions from peatlands represent ≈10% of the total methane flux to the atmosphere. Under projected climate change scenarios, peats are expected to increase their contribution to atmospheric CH_4. Methane is produced by methanogenic microorganisms in the permanently saturated lower layers of peat while it is consumed by methanotrophic microorganisms primarily in the upper aerobic layers. An understanding of the mechanisms for the mediation between methanogenic and methanotrophic activities is crucial to fully comprehend the processes that abate CH_4 emissions from peatland. This project aims to develop and assess a unique and novel stable isotope tool to elucidate how the carbon isotopic signature of a methanotroph biomarker, diploptene, is associated to methane availability as a carbon source in peat

Methodology

Compound-specific stable isotope analysis (CSIA) is transforming environmental research, as evidenced by the exponential increase since 1995 in citations of peer-reviewed papers using the technique (i.e. 1500 to ~14,000). Notably, carbon CSIA has been employed to elucidate processes of microbial-mediated CH_4 release from soils/peat in modern and ancient environments.



Diploptene is a methanotroph membrane lipid, which concentration, we demonstrated recently, linearly increases with methane emission. Additionally, its carbon stable isotopic values ($\delta^{13}C$) were also shown to correlate with both methane production and consumption and to change in response to the source of methane.

The $\delta^{13}C$ signature of diploptene found in peat bogs tends to be ca. −30‰ and −40‰; and although depleted compared to other organic material, it is enriched compared to the ca. -60‰ of biogenic methane, therefore not directly representative of the source methane. Various factors could be responsible for the offset in these values. To further develop the use of diploptene as a biomarker for methane oxidation, it is crucial to understand how its $\delta^{13}C$ is

related to the $\delta^{13}C$ of the possible carbon sources and particularly methane. This project will assess how the $\delta^{13}C$ values of individual carbon atoms within the molecule contribute to the overall signature preserved in the environment through the development of an on-line position specific stable isotope analysis method for diploptene and its use for the characterisation of both planned cultures and field samples.

I- Method development of on-line PSIA for diploptene

The study of *intra*molecular isotopic variations in a molecule is termed position specific stable isotope analysis (PSIA). We have developed a novel and unique system for on-line PSIA: after being purified on-line by gas chromatography, compounds of interest are pyrolysed into smaller compounds and the $\delta^{13}C$ values of the fragments are determined. Control in the system over the pyrolysis temperature and reaction time means that the pyrolysis can be optimised for selection of the fragments that are the most meaningful to a given application. For diploptene, it is expected that pyrolysis at low temperatures should first break off the CH_3 groups from the ringed backbone to produce methane. On-line PSIA has therefore the potential to unveil the $\delta^{13}C$ values of these groups and help in explicitly determining the origin of different isotope values of diploptene. Method development will involve optimising the pyrolysis conditions for selection and characterisation (using ^{13}C labelled diploptene samples) of the pyrolysis fragments most relevant to the research question.

II- Analysis of planned culture and field peat samples

Firstly, the student will perform growth experiments on methanotroph cultures grown under different conditions, such as high/low methane, high/low oxygen, high/low nitrogen, high/low copper… The changes in the CSIA and PSIA $\delta^{13}C$ of diploptene will be monitored. The student will be trained and work for a portion of the time in co-supervisor Prof. David Graham's lab.

Secondly, the student will collect modern peat samples from the aerobic section of a Scottish peatland, Black Law, and analyse the CSIA and PSIA $\delta^{13}C$ values of diploptene. Black Law is an ideal site for collection of natural samples for comparison with the laboratory cultures, because methane efflux, water table depth and a suite of other metadata are available to help with results analysis.

The combination of comprehensive stable isotope data for planned cultures and field samples will provide unique and crucial insights to the assimilation of source CH_4 in lipid biomarkers and the information it provides about the CH_4 flux.

Timeline

First 18 months:

Literature review and theoretical and technical training in analytical chemistry, stable isotope analysis, molecular fossils analysis and metabolic microbiology.
Development of an on-line PSIA method for the methanotroph biomarker diploptene. (University of Glasgow)

Second 18 months:

Growth experiments on methanotroph cultures for compound and position specific analysis of diploptene. (Newcastle University)
Collection of modern peat samples from the aerobic section of a Scottish peatland for compound and position specific stable isotope analysis of diploptene. (University of Glasgow)

Final 6 months:

Thesis preparation and further publications.

Training & Skills

This project provides an excellent opportunity for interdisciplinary training of a PhD student in the latest organic geochemistry, biomarker, and environmental microbiology techniques. Furthermore, the University of Glasgow provides a supportive environment with access to numerous career development opportunities, including: weekly workshops and seminars that provide training in oral presentations, manuscript writing and review, grant writing and more. Upon completion the candidate will be marketable for a wide range job opportunities ranging from palaeoclimate research to environmental engineering.

References & Further Reading

Echoes of Life – What fossil molecules reveal about Earth history. Gaines, Eglinton, and Rullkötter, 2009. Oxford Press. pp. 355

Kip et al. (2010) *Nature Geoscience*, doi:10.1038/ngeo939

Gauchotte et al. (2009) *RCM,* doi:10.1002/rcm.4222

Carbon Landscapes
http://www.carbonlandscapes.co.uk

Global Carbon Project
http://www.globalcarbonproject.org/methanebudget/

Further Information

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