DEVELOPMENT AND APPLICATION OF BIOMARKER PROXIES FOR TERRESTRIAL METHANE CYCLING

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Introduction

Atmospheric methane (CH_4) is an important greenhouse gas and the dominant natural source is terrestrial wetlands (~80% of total natural CH_4 emissions). Despite its importance in the climate system, our understanding of past CH_4 concentrations is limited and there are no proxy methods to reconstruct ancient CH_4 emissions beyond the reach of the Antarctic ice cores. Previous studies suggest the carbon isotopic composition ($\delta^{13}C$) of bacterial hopanoids can be used to infer relative changes in terrestrial CH_4 cycling. For example, a decrease in the $\delta^{13}C$ value of bacterial hopanes during the onset of the Paleocene-Eocene Thermal Maximum (PETM; ~56 million years ago) within the Cobham (UK) lignite indicates the consumption of isotopically light CH_4 by aerobic methanotrophs (Pancost et al., 2007).

Despite this initial success, the environmental controls regulating the carbon isotopic composition of hopanoids in modern (and ancient) wetland settings remains poorly constrained. Here we undertake an unprecedented global survey of hopanoid $\delta^{13}C$ values in a range of peat-forming environments (n = >100 samples from 13 globally widespread sites), spanning a wide temperature (~5 to 28°C) and pH (~3 to 8) range. Guided by these results, we re-interpret and generate new records of terrestrial methane cycling from a suite of marginal marine deposits spanning the PETM.

Results & Conclusions

1. Modern peatlands

In our global compilation of modern peat, bacterial hopane/hopene distributions are dominated by diploptene or the C_{31} 17α,21β(H) homohopane. The latter has been attributed to rapid isomeric catalysation at the C-17 position as a result of acidic conditions. Our global compilation is consistent with this hypothesis rather than a temperature control on isomerisation; however, other factors could drive subtle downcore variations.

Our results indicate a statistically significant correlation ($p < 0.05$) between modern hopane $\delta^{13}C$ values and mean annual air temperature (Fig 1.a). In temperate peatlands, the $\delta^{13}C$ value of C_{31} hopanes range from -22 to -26‰ and do not capture a strong methanotroph signal. This is consistent with recent work which suggests that heterotrophic organisms are the dominant hopanoid producers in peat (Talbot et al., 2016). In tropical peatlands, C_{31} hopanes are increasingly ^{13}C-depleted, ranging between -30 to -32‰. Increasing ^{13}C-depletion with increasing temperature can be attributed to either: 1) enhanced methanogenesis and therefore greater methane oxidation and/or 2) enhanced respiration and greater utilisation of recycled CO_2 by photoautotrophs.

Our results also provide evidence for incorporation of methane or recycled CO_2 into tropical peat-forming plants, via ^{13}C-depletion mid-chain *n*-alkanes (relative to long-chain *n*-alkanes;

Fig 1.b). The occurrence of *Sphagnum*-associated methanotrophy has previously been shown in living *Sphagnum* moss species (van Winden et al., 2010). However, this is the first evidence that this signal is preserved in the sedimentary record and could provide a complementary tool for tracing wetland methane cycling.

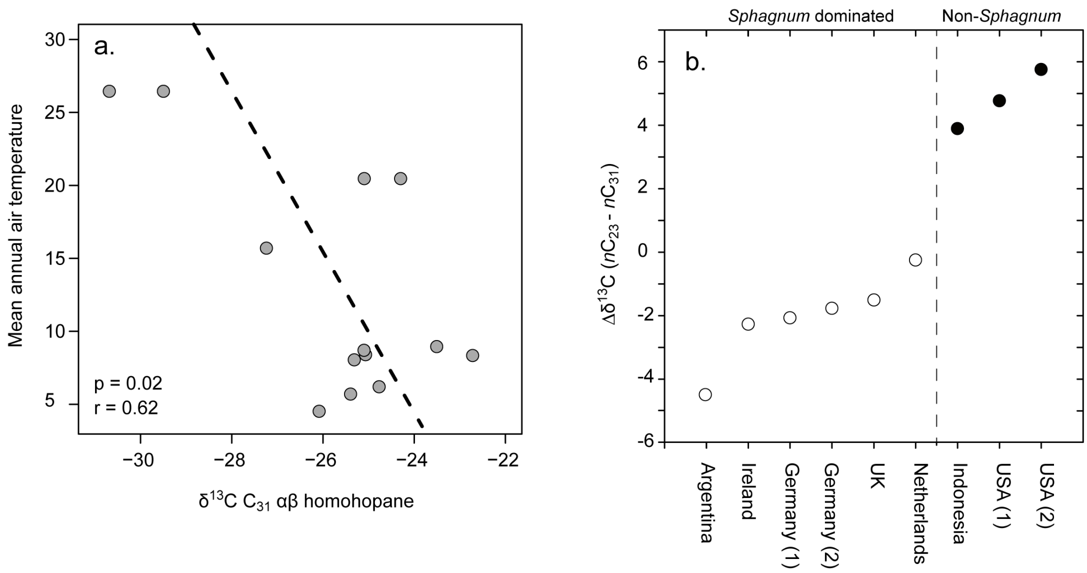

Figure 1: a) $\delta^{13}C$ value of the C_{31} 17α,21β(H) homohopane vs. mean annual air temperature in acidic, ombrotrophic bogs. b) $\delta^{13}C$ offset between mid-chain and long-chain n-alkanes for Sphagnum and non-Sphagnum dominated peatlands.

2. Application to ancient peatlands

In the modern dataset the lowest hopane $\delta^{13}C$ value is –35‰, much higher than those observed during the PETM with values < -60‰ (e.g. Pancost et al., 2007). To explore whether the extremely depleted hopane $\delta^{13}C$ values observed at Cobham (UK) are unique or common during the PETM, hopane $\delta^{13}C$ values were obtained from two other sections spanning the PETM; the Otaio section from New Zealand and the Recito Mache section from Venezuela. Both sections exhibit ^{13}C-depleted hopanes (-40 to -60‰) and a negative carbon isotope excursion (10 to 30‰) associated with the PETM. These extremely depleted values provide further evidence for enhanced methane cycling during past carbon cycle perturbations. These extremely depleted hopane $\delta^{13}C$ values observed around the world during the PETM are much lower than those found in any modern wetlands, suggesting that we have yet to find the modern analogue for the environmental conditions that occurred in PETM wetlands.

References

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