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Insoluble prokaryotic membrane lipids in a *Sphagnum* peat: Implications for organic matter preservation

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ABSTRACT

Preservation of organic matter (OM) in the geosphere has a direct impact on carbon bioavailability, the carbon cycle and the formation of fossil fuels. We have examined some of the processes that lead to the preservation of OM by characterising insoluble OM in a *Sphagnum* peat bog. We focussed on the partitioning of prokaryotic biomarkers between solvent-extractable and insoluble OM fractions and how that partitioning changed with depth. The insoluble organic matter (IOM) was examined using stepwise chemical degradation involving base and acid hydrolysis. *Iso-* and *anteiso*-C_{15} and C_{17} fatty acids (FAs), hopanoic acid and bishomohopanol, and branched glycerol dialkyl glycerol tetraethers (GDGTs) – diagnostic for Bacteria – were targeted as well as archaeol and isoprenoidal GDGTs – diagnostic for Archaea. High percentages of these compounds – up to 65% – occur in IOM pools, indicating that archaeal- and bacterially derived OM is prone to insolubilization even in shallow sediments (<5 cm depth). Differences in functionalities – likely related to intact polar (IP) head groups – seem to determine the insolubilization of prokaryotic lipids; specifically, we propose that compounds bearing rapidly degradable phosphate-based polar head groups are less likely to be incorporated into the insoluble OM pools. Collectively, these data indicate that microbial membrane lipids are rapidly incorporated into peat IOM during early diagenesis. We suggest that this is due to an inherently recalcitrant character of some prokaryotic cells which affords protection to their membrane lipids. However, this large proportion of insoluble prokaryotic lipids does not appear to be entirely stable at shallow burial depths, indicating that the peat IOM is a dynamic reservoir, at least during early diagenesis.

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1. Introduction

Most of the organic matter (OM) produced in the biosphere is remineralized to its inorganic constituents (e.g., Berner, 1989; Le Berre et al., 1991; Harvey, 2006; Eglinton, 2012), such that only 0.5–1% of global primary productivity is preserved in the geosphere (Le Berre et al., 1991; Eglinton, 2012). Numerous workers have contributed to the understanding of OM preservation in the geosphere, with much work showing that under the appropriate conditions even highly reactive compounds such as saccharides can be preserved (e.g., Sinninghe Damsté et al., 1998; Kok et al., 2000; van Dongen et al., 2006). Some studies have emphasised the link between biomacromolecules, such as cell walls of algae and bacteria (Philp and Calvin, 1976), algaenans (Largeau et al., 1984, 1986; Derenne et al., 1988), cutans (Nip et al., 1986a,b, 1989), suberans (Tegelaar et al., 1989a,b) and lignins (Stach and Murchison, 1982), to degraded analogues in the sediment. This indicates that OM preservation is partially driven by the selective preservation of resistant biomacromolecules (Tegelaar et al., 1989a,b). Conversely, Tissot and Welte (1984) argued that OM preservation arises from the protection afforded by a three dimensional geomacromolecule formed by successive condensation reactions of degraded biomolecules over time. Sinninghe Damsté and de Leeuw (1990) highlighted a particular suite of such condensation reactions, whereby free hydrogen sulfide and sulfur-bearing molecules promote geomacromolecule formation via sulfur cross-linking. Cross-linking reactions have also been proposed to occur via ether/peroxide bonds in the presence of oxygen most likely via radical reactions (Harvey et al., 1983; Versteegh et al., 2004; de Leeuw, 2007; Gupta et al., 2007). In any case – selective preservation of biomacromolecules or geomacromolecule formation over time – the fact that OM is insoluble or non-extractable with standard organic solvent-based extractions (e.g., Largeau et al.,

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1984, 1986; Derenne et al., 1988; Tegelaar et al., 1989a) or becomes insoluble (e.g., Harvey et al., 1983; Tissot and Welte, 1984; Sinninghe Damsté and de Leeuw, 1990; Versteegh et al., 2004), seems to play a crucial role in its preservation (Durand, 1980; Tissot and Welte, 1984). Yet environmental factors have also been proposed as the controlling factors of OM fate (e.g., Marín-Spiotta et al., 2014).

Diagnostic molecules, such as prokaryotic membrane lipids, can be targeted in the fractions obtained from insoluble OM (IOM) chemical degradation. The diagnostic structures of many prokaryotic membrane lipids facilitate their identification in different OM pools, as opposed, for example, to lipids that occur as both free compounds and building blocks of biomacromolecules (e.g., C_{16} and C_{18} FAs). Previous studies have reported the occurrence of prokaryotic biomarkers in IOM fractions. For example, Otto and Simpson (2007) identified *iso*-C_{16} and C_{18} FAs – whose branched chain largely confirms their bacterial origin (Kaneda, 1991) – in base hydrolysates of post solvent-extraction residues, when characterising soil OM from a grassland-forest transition zone in Canada. Analogously, hopanoids have been reported to occur in the IOM of a wide range of settings when studying recalcitrant OM structure and composition. For example, numerous studies focused on the characterisation of kerogen have revealed hopanoids after pyrolysis (Gallegos, 1975; Seifert, 1978; Love et al., 1995; Berwick et al., 2010; Pan et al., 2010), desulfurization (Hofmann et al., 1992; Richnow et al., 1992; Adam et al., 1993) and other chemical degradation methods such as oxidation with sodium dichromate (Barakat and Yen, 1990) or catalytic hydrogenolysis (Mycke et al., 1987). The occurrence of hopanoids in the IOM of other settings has also been reported; for example, after pyrolysis of lacustrine sediments and Norwegian fjords (Farrimond et al., 2003) and humic substances (Poerschmann et al., 2007) and after alkaline hydrolysis of marine surface sediments (Barouxis et al., 1988). Finally, GDGTs or degraded counterparts, i.e. biphytanyl chains, have also been identified in IOM pools. In the seventies studies of kerogen structure and composition applied a wide range of chemical degradation approaches, such as chromic and permanganate oxidation (Simoneit and Burlingame, 1973), pyrolysis (Gallegos, 1975), ozonolysis (van den Berg et al., 1977) and ether cleavage (Michaelis and Albrecht, 1979); many of these, especially ether cleavage approaches, released the biphytanyl components of GDGTs. More recently, interest in GDGTs has been revived by their utility in paleoclimate reconstruction (see Schouten et al., 2013 and Refs. therein), and they have been identified in the IOM from a variety diversity of settings. They have been reported to occur in black shales (Kuypers et al., 2002) after oxidation with ruthenium tetroxide, in marine sediments after pyrolysis (Pancost et al., 2008) and acid and base hydrolysis (Weijers et al., 2011), and in peat bogs and podzols after acid hydrolysis (Huguet et al., 2010a,b). The majority of recent studies target GDGTs because of their utility in paleoenvironmental investigations; however, overall these studies clearly reveal the potential for using diagnostic prokaryotic lipids as tracers for how specific chemical motifs occur in insoluble sedimentary OM during diagenesis.

In the current study, prokaryotic membrane lipids are first solvent-extracted and then released from IOM fractions via a stepwise selective chemical degradation of a *Sphagnum* peat, with the aim of assessing IOM composition and formation. We determined the concentrations of a range of such lipids – including *iso*- and *anteiso*-C_{15} and C_{17} fatty acids (branched FAs), hopanoic acid and bishomohopanol, archaeol and both branched (br-) and isoprenoid (i-) glycerol dialkyl glycerol tetraethers (GDGTs) – in solvent extractable fractions as well as those released after chemical degradation (non-extractable or insoluble). This approach allows us to interrogate the degree to which relatively labile compounds are incorporated into peat IOM. Additionally, it provides insights into the geomicrobiology of the setting and constrains how such biomarkers can be applied in future investigations.

2. Methods

2.1. Samples

A peat core was collected from Cors Crymlyn peatland in Swansea, Wales. According to the core management plan of the Countryside Council for Wales (CCW, 2010), this bog is part of a special area of conservation (SAC), which comprises two component sites of special scientific interest, Cors Crymlyn/Crymlyn Bog and Pant-y-Sais, which together cover an area of ca. 300 hectares. All of Pant-y-Sais, except for the adjoining Tennant Canal, and approximately one-third of Crymlyn Bog, has been declared to be a National Nature Reserve (NNR; Pant-y-Sais). Rosen and Dumayne-Peaty (2001) dated Cors Crymlyn using radiocarbon and ^{210}Pb, from which it is inferred that the 80 cm core used for the current research is probably ca. 500–600 years old in the deepest layers. The core was sampled in an area where the dominant vegetation is *Sphagnum* moss, *Typha latifolia* and *Juncus effusus* (Bevan, J., pers. comm.).

The core analysed had a cross sectional area of 10×10 cm, and 80 cm length. The water table was at about 15 cm depth, below which anoxic conditions are inferred to occur. The poor drainage in the setting promotes anoxic conditions and acidity, enhancing OM preservation (Dean and Gorham, 1998). After collection, the peat core was stored at 15 °C. Prior to analysis the core was sliced into ca. 1 cm sections from 5, 25, 55, 70 and 80 cm depth; sections were freeze-dried and stored at −20 °C.

2.2. Experimental procedure

Freeze-dried peat sections were finely ground, and an aliquot of each depth section was subjected to elemental analysis to determine total carbon (TC) content (Carlo Erba EA1108 elemental analyser); additionally, total inorganic carbon (IC) was determined using a modified Strohlein Coulomat 702 analyser. TOC (%) was calculated as the difference between TC and TIC.

Five horizons from the Cors Crymlyn peat core were subjected to sequential solvent-extractions and a selective chemical degradation of the post-extraction residue (Fig. 1). First, a modified Bligh and Dyer extraction was performed (details below) to obtain to the corresponding total lipid extract (E1BD) and the post-extraction residue (R1BD). Subsequently, R1BD was subjected to Soxhlet extraction, from which E2Sox and R2Sox were obtained. Biomarkers obtained in E1BD and E2Sox are considered extractable biomarkers as opposed to those obtained after chemical degradation. Aliquots of E1BD and E2Sox total lipid extracts were either acid hydrolysed or subjected to column chromatography. The final post-extraction residue, R2Sox was subjected to a selective chemical degradation, consisting of a base hydrolysis – obtaining E3BHy and R3BHy – followed by acid methanolysis of R3BHy to obtain E4AMe and R4AMe. Biomarkers contained within E3BHy and E4AMe are considered non-extractable or insoluble biomarkers (nominally part of the insoluble organic matter, IOM).

2.2.1. Modified Bligh and Dyer extraction

The modified Bligh and Dyer extraction (BD; adapted from Bligh and Dyer, 1959) was performed upon freeze-dried samples. BD extraction was applied due to the nature of our sediments, recently formed (<600 years old, Rosen and Dumayne-Peaty (2001)) peaty soil; and it is commonly used in the investigation of microbial

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