Organic Geochemistry 67 (2014) 8–18

Contents lists available at ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem

Autotrophic and heterotrophic associated biosignatures in modern freshwater microbialites over seasonal and spatial gradients

Allyson L. Brady [a,1], Bernard Laval [b], Darlene S.S. Lim [c,d], Greg F. Slater [a,*]

[a] School of Geography and Earth Sciences, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4L8, Canada
[b] Department of Civil Engineering, University of British Columbia, 2002-6250 Applied Science Lane, Vancouver, British Columbia V6T 1Z4, Canada
[c] Mail-Stop 245-3, NASA Ames Research Center, Moffett Field, CA 94035, USA
[d] SETI Institute, 189N Bernardo Avenue, Mountain View, CA 94043, USA

ARTICLE INFO

Article history:
Received 22 May 2013
Received in revised form 22 November 2013
Accepted 27 November 2013
Available online 5 December 2013

ABSTRACT

Phospholipid fatty acid (PLFA) profiles and isotopic biosignatures associated with autotrophic and heterotrophic microbial processes in freshwater microbialites exposed to seasonal and spatial gradients in Pavilion Lake, British Columbia were investigated. The PLFA biosignature profiles of the microbialite associated microbial communities were dominated by saturated and monoenoic PLFAs and showed no resolvable response to variation in light or temperature down to a water depth of 33 m and across seasons. Microbialite mean $\delta^{13}C_{org}$ values ($-26.0 \pm 3.8‰$) and $\Delta\delta^{13}C_{DIC\text{-}org}$ discrimination of ca. 25‰ supported non-CO_2 limited photosynthesis. More abundant and ^{13}C-depleted PLFAs ($\Delta\delta^{13}C$ 7–14‰ vs. bulk organic matter) were indicative of autotrophic microbes. Less abundant and ^{13}C-depleted PLFAs ($\Delta\delta^{13}C$ 3–4‰) were indicative of heterotrophic organisms, particularly branched (*iso*/*anteiso*15:0 and 10me16:0) PLFAs. Dark coloured microbialites from the bottom of the lake (below 46 m water depth) had comparatively low biomass and a higher proportion of branched PLFAs, including biomarkers for sulfate reducing bacteria. Bulk $\delta^{13}C_{carb}$ values of microbialite carbonate at 6 and 11 m water depth were up to ca. 2‰ more ^{13}C enriched than the value predicted for precipitation from ambient dissolved inorganic carbon and had increased biomass in summer, indicating a preserved biosignature of photosynthetic activity. Other $\delta^{13}C_{carb}$ values were generally within the range predicted for equilibrium precipitation. Estimated precipitation temperature values from $\delta^{18}O_{carb}$ were consistent with measured late summer water values. While both autotrophic and heterotrophic processes occurred at all depths, preservation of an enriched ^{13}C biosignature was only detected at shallow depths where photosynthetic activity and biomass production were relatively high.

Introduction

Microbial communities have been proposed to play an important role in microbialite formation through sediment trapping and binding (Stolz et al., 2001), as nucleation sites for crystal growth (Bosak and Newman, 2003) and/or by influencing geochemical conditions, causing in situ precipitation (Merz-Preiß and Riding, 1999; Merz-Preiß, 2000; Reid et al., 2000). However, abiotic models of microbialite formation have also been proposed (e.g. Grotzinger et al., 2000). The role of biology and the relative importance of autotrophic vs. heterotrophic processes in microbialite formation can be unclear. Identifying unambiguous biosignatures of microbial activity is difficult, in part due to environmental and microbial community variation between locales (Grotzinger and Knoll, 1999; also see Dupraz et al., 2009 for an overview). Modern microbialites with varying morphology occur at differing water depths in freshwater Pavilion Lake, British Columbia, Canada. This morphological variation has been hypothesized to relate to differences in biological activity in response to change in light level at different water depths (Laval et al., 2000), providing an opportunity for investigating the relative importance of microbial autotrophy vs. heterotrophy in their formation.

Both photosynthesis and heterotrophic metabolic activity, such as sulfate reduction, have been linked to carbonate precipitation (Merz, 1992; Canfield and Des Marais, 1993; Visscher et al., 2000; Ludwig et al., 2005; Baumgartner et al., 2006). Microbial metabolic activity can influence the isotopic composition of dissolved inorganic carbon (DIC) and precipitation of carbonate from this DIC can preserve the isotopic effects as a biosignature (Merz, 1992; Sumner, 2001; Andres et al., 2006; Brady et al., 2010). In order to be identified, microbial activity must induce deviation in measured carbonate $\delta^{13}C$ values that are outside the range of values predicted for equilibrium (abiotic) precipitation. Biosignatures

* Corresponding author. Tel.: +1 905 525 9140x26388.
E-mail address: gslater@mcmaster.ca (G.F. Slater).
[1] Present address: Department of Biological Sciences, University of Calgary, 2500 University Drive N.W., Calgary, Alberta T2N 1N4, Canada.

0146-6380/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.orggeochem.2013.11.013

of photosynthetic activity have been recognized in DIC and carbonate enriched in ^{13}C in Pavilion Lake (Brady et al., 2010), in small stromatolites and thrombolites from nearby Kelly Lake (Ferris et al., 1997) and others (e.g. Hollander and McKenzie, 1991; Merz, 1992; Thompson et al., 1997; Hodell et al., 1998). In contrast, input of ^{13}C-depleted CO_2 to the aqueous microenvironment derived from oxidation of ^{13}C-depleted organic matter (OM) by heterotrophic bacteria, e.g. sulfate reducing bacteria (SRB), has led to an overall decrease in the ^{13}C content of DIC and associated carbonate (Sumner, 2001; Andres et al., 2006). The resulting isotopic biosignature and its relationship to the predicted equilibrium carbonate $\delta^{13}C$ values, reflect the balance of autotrophic to heterotrophic processes. Isotopic signatures of this balance may also be reflected in the distribution of microbial phospholipid fatty acids (PLFAs) and the offset between the PLFA isotopic composition and the isotopic composition of bulk cell OM. While variability exists depending upon the microbe and metabolism (see Hayes, 2001 for an overview), a large offset (ca. 7–9‰) is generally associated with phototrophic organisms (Sakata et al., 1997; Jahnke et al., 2004) while a relatively smaller offset (ca. 2–4‰) tends to be associated with heterotrophic organisms (Blair et al., 1985; Abraham et al., 1998; Teece et al., 1999; Londry et al., 2004). Furthermore, individual PLFAs or classes of PLFAs have been linked to certain microbial groups (Vestal and White, 1989; Rajendran et al., 1995; White et al., 1996; Zelles, 1999; Green and Scow, 2000) and the distribution of PLFAs associated with microbialites also provides a means of characterizing the microbial community.

Modern microbialites are the closest analogues of fossilized stromatolites for investigating biotic mechanisms of formation and biosignatures of autotrophy and heterotrophy. Microbial mats associated with microbialite surfaces are diverse communities composed of autotrophic and heterotrophic microbes, including eukaryotes, cyanobacteria, aerobic heterotrophs and SRB (e.g. Reid et al., 1995; Burns et al., 2004; Foster et al., 2009; Nitti et al., 2012). While photosynthetic algae and cyanobacteria have been shown to play a significant role in the formation of some modern microbialites (Ferris et al., 1997; Reid et al., 2000), studies have also identified heterotrophy as an important mechanism contributing to carbonate precipitation in freshwater microbialites from Cuatro Ciénegas, Mexico (Breitbart et al., 2009) and in marine microbialites from the Exuma Cays, Bahamas (Visscher et al., 1998, 2000; Andres et al., 2006). In previous work, carbonate enriched in ^{13}C was identified as a biosignature of autotrophy as an important process promoting precipitation within surface nodular communities associated with the Pavilion Lake microbialites (Brady et al., 2010). However, the nodular communities make up only a relatively small component of the microbial communities associated with these microbialites and are not present on all structures. As microbial activity changes with environmental parameters such as light level, temperature and geochemical environment (Jørgensen et al., 1988; Bebout and Garcia-Pichel, 1995; Fritsen and Priscu, 1998), this biosignature may not be consistently present and/or dominant. Variation in the microbial community over a spatial or seasonal scale may lead to the formation of both autotrophic and heterotrophic isotopic biosignatures in different structures within a microbialite system or within an individual microbialite. For example, a vertical profile within the top 2–3 cm of mat covering an individual microbialite from Cuatro Ciénegas, Mexico showed variation in microbial diversity and $\delta^{13}C$ values, reflecting a change from a surface phototrophic community to a heterotrophic dominated one deeper within the mat (Nitti et al., 2012). To our knowledge, no studies have addressed the variability in biosignatures of autotrophy and/or heterotrophy within a microbialite system that undergoes seasonal environmental fluctuation and exists across a range of depth environments or within individual microbialite structures that exhibit distinct colour zonation. Freshwater microbialites in Pavilion Lake represent an opportunity to assess the presence of biosignatures of microbial activity in both the active microbial community via PLFAs and within carbonates that have the potential for long term preservation.

2. Sampling location and analytical methods

2.1. Pavilion Lake microbialites

Pavilion Lake is in south-central British Columbia, Canada, ca. 450 km northeast of Vancouver. This relatively small (5.7 km × 0.8 km and 65 m deep), temperate, freshwater and ultra-oligotrophic lake, with a pH of ca. 8.3, hosts microbialites ranging from several cm to m in height with varying morphology between water depths of ca. 10 and 50 m (Laval et al., 2000; Lim et al., 2009). The bottom of the lake slopes steeply to 35 m, after which it slopes more gradually to a maximum recorded depth of 65 m. Microbialites from intermediate depth (ca. 20–30 m) are more cohesive and generally larger than more porous ones from shallower depth (ca. 10–20 m). Microbialites at the deepest depths (ca. 50 m) in the middle of the central basin (N 50°51.932′ W 121°44.333′) are very dense and have a black coating. Although microbialite morphological variation shows a trend with depth (Fig. 1), it is not clear which factors – physical, chemical or biological – influence the overall morphology of the structures (Laval et al., 2000; Lim et al., 2009). The majority of the microbial community is present as a mat ca. 5 mm thick covering most of the outer surface of the microbialites, composed of photosynthetic cyanobacteria including *Synechococcus* spp., *Pseudanabaena* spp. and *Oscillatoria* spp., diatoms and heterotrophic microbes (Laval et al., 2000). This study focusses on the surface microbial mat and associated isotope signatures vs. a previous study (Brady et al., 2010) that examined distinct nodules composed predominantly of filamentous cyanobacteria that exhibited a biosignature of photosynthesis.

2.2. Microbialite and water chemistry collection and characterization

2.2.1. Seasonal and depth sampling

Sampling of microbialites was performed by SCUBA divers 2–5 times a year between 2004 and 2008. Several sets of microbialite samples were collected to represent seasonal timescales, depth profiles and visually distinct colour zones on individual microbialites. All microbialite depths are reported as water depth relative to the lake surface. To determine the extent of variability in PLFA distribution between individual microbialites from the same depth, triplicate samples of adjacent microbialites were collected from 11 m during a single sampling period. A temporal series was collected to assess seasonal variation. These samples were collected at two water depths (11 and 26 m) representative of two of the major microbialite morphologies in the lake (Fig. 2; Laval et al., 2000). Samples were collected maximally 5 times a year: winter (W, February), spring (Spr, April), early summer (ES, early June), late summer (LS, late July or early August) and the fall (F, October). In addition, representative microbialite samples were collected during the summer from water depths ranging from 6 to 52 m to investigate potential variability with depth. Intact microbialites were brought to the surface and immediately frozen on-site and transported to McMaster University on dry ice prior to lyophilisation and further analysis.

Water samples for ^{13}C and ^{18}O analysis were collected in crimp sealed glass serum bottles with no headspace and fixed with $HgCl_2$. Photosynthetically active radiation (PAR) was measured during summer using a LI-COR PAR sensor attached to a conductivity-temperature-depth (CTD) profiler. Water temperature was measured