Earth and Planetary Science Letters 441 (2016) 52–59

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Examining Archean methanotrophy

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ARTICLE INFO

Article history:
Received 1 October 2015
Received in revised form 10 January 2016
Accepted 5 February 2016
Editor: D. Vance

Keywords:
stromatolite
C isotopes
clumped isotopes
anaerobic oxidation of methane
reductive acetyl-CoA pathway

ABSTRACT

The carbon isotope ratios preserved in sedimentary rocks can be used to fingerprint ancient metabolisms. Organic carbon in Late Archean samples stands out from that of other intervals with unusually low $\delta^{13}C$ values (~−45 to −60‰). It was hypothesized that these light compositions record ecosystem-wide methane cycling and methanotrophy, either of the aerobic or anaerobic variety. To test this idea, we studied the petrography and carbon and oxygen isotope systematics of well-known and spectacular occurrences of shallow water stromatolites from the 2.72 Ga Tumbiana Formation of Western Australia. We examined the carbonate cements and kerogen produced within the stromatolites, because methanotrophy is expected to leave an isotopic fingerprint in these carbon reservoirs. Mathematical modeling of Archean carbonate chemistry further reveals that methanotrophy should still have a discernible signature preserved in the isotopic record, somewhat diminished from those observed in Phanerozoic sedimentary basins due to higher dissolved inorganic carbon concentrations. These stromatolites contain kerogen with $\delta^{13}C_{org}$ values of ~−50‰. By microsampling different regions and textures within the stromatolites, we determined that the isotopic compositions of the authigenic calcite cements show a low degree of variation and are nearly identical to values estimated for seawater at this time; the lack of low and variable $\delta^{13}C_{carb}$ values implies that methanotrophy does not explain the low $\delta^{13}C_{org}$ seen in the coeval kerogen. These observations do not support a methanotrophy hypothesis, but instead hint that the Late Archean may constitute an interval wherein autotrophs employed markedly different biochemical processes of energy conservation and carbon fixation.

1. Introduction

It is widely recognized that organic matter contained in sedimentary successions of Late Archean age (circa 2.5 to 2.9 Ga) has unusually ^{13}C-depleted isotopic compositions ($\delta^{13}C_{org}$ ~−45 to −60‰ PDB) compared to younger intervals (Phanerozoic $\delta^{13}C_{org}$ ~−22 to −32‰ PDB) (Eigenbrode and Freeman, 2006; Fischer et al., 2009; Schoell and Wellmer, 1981; Thomazo et al., 2009). From its discovery in ultra-mature Late Archean kerogens from the Superior Province and the Tumbiana Formation of the Fortescue Group, Western Australia, it was hypothesized that this isotopic signal reflects the enhanced paleoenvironmental cycling of methane (Hayes, 1994; Schoell and Wellmer, 1981).

Oxidation and assimilation of methane by methanotrophic organisms yields exceptionally ^{13}C-depleted biomass. Recognizing this, Hayes (1994) introduced the concept of a Late Archean "Age of Global Methanotrophy", to explain the $\delta^{13}C$ values seen in Archean organic matter. This was originally envisioned as aerobic methanotrophy (Hayes, 1994), but later based on two discoveries—microbial consortia capable of anaerobic oxidation of methane (AOM) in modern anoxic environments (Boetius et al., 2000) and the widespread mass independent fractionation of sulfur isotopes in Archean basins (Farquhar et al., 2000)—Hinrichs (2002) updated the idea to include AOM, expanding on a point made similarly by Schoell and Wellmer (1981) on the basis of modern sedimentary pore fluid biogeochemical profiles. By comparing accumulation rates of methane oxidation from modern methane seeps, anoxic coastal sediment, and the Tumbiana Formation, Hinrichs (2002) showed that AOM processes could reasonably explain the Archean isotopic signal, possibly even under the condition of lower seawater sulfate concentrations. Subsequent studies developed biogeochemical variations on this theme again involving oxygenic photosynthesis or anoxygenic photosynthetic pathways, but these hypotheses all draw on abundant ecosystem methanotrophy in large part to explain the ^{13}C-depleted kerogen, with the disappearance of this isotopic signal in younger Precambrian strata due to either a decline in atmospheric methane or changes in the relative abundance of electron acceptors for methanotrophy (Coffey et al., 2013;

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http://dx.doi.org/10.1016/j.epsl.2016.02.013
0012-821X/

Eigenbrode and Freeman, 2006; Stüeken et al., 2015; Thomazo et al., 2009; Yoshiya et al., 2012).

Despite its attractiveness, there are several outstanding issues with the global methanotrophy hypothesis that could benefit from further testing. 1) While substantially more ^{13}C-depleted than expected by carboxylation from the Calvin cycle, the isotopic composition of Late Archean organic matter is not unique for methanotrophs and is consistent with other biochemical pathways (Blaser et al., 2013; Fischer et al., 2009; Gelwicks et al., 1989). 2) Sulfate levels may have been sufficiently low as to greatly limit the extent of sulfate reduction-driven AOM in Late Archean marine basins (Crowe et al., 2014), though methane oxidation might have been instead accomplished anaerobically via ferric iron phases (Beal et al., 2009) or high-valent nitrogen-bearing compounds (Haroon et al., 2013). Finally, 3) existing data from Archean carbonates with exceptionally low $\delta^{13}C_{org}$ values do not host isotopic and textural features one might expect of carbonates produced in environments of prevalent methanotrophy.

Fortunately, environments in which methanotrophy is a principal part of the carbon mass flux leave isotopic signatures not just in the organic phases present, but also in the carbonate phases produced; this forms the logic for an approach to test the global methanotrophy hypothesis. Both aerobic methanotrophy and AOM increase dissolved inorganic carbon (DIC) in the environment and strongly alter the carbon isotope ratios by adding isotopically light DIC. Furthermore, AOM also generates a strong flux of alkalinity and thus promotes the precipitation of carbonates as described by the following net reaction: $CH_4 + SO_4^{-2} + Ca^{+2} \rightarrow CaCO_3 + H_2S + H_2O$ (Michaelis et al., 2002). Authigenic carbonates formed by methanotrophic processes have been widely observed in modern marine sediments (e.g. Luff and Wallmann, 2003; Marlow et al., 2014) and can be readily preserved in the geological record where they have been recognized on the basis of isotopic and textural features in Phanerozoic strata, and perhaps as old as 635 Ma (Bristow and Grotzinger, 2013; Peckmann and Thiel, 2004). AOM creates both carbonate and organic matter with remarkably low δ^{13}C values (Bristow and Grotzinger, 2013) (Table S1). We compiled a comprehensive C isotope dataset from AOM sites preserved in Phanerozoic basins (Table S1); the data illustrate that $\delta^{13}C_{carb}$ values can be down to −59‰ and $\delta^{13}C_{org}$ values can be as low as −133‰, with typical δ^{13}C values both substantially more variable and much lower overall than Archean values.

To test the methanotrophy hypothesis, we closely examined the petrographic textures and isotopic compositions of kerogen and authigenic carbonate cements in stromatolites collected from the Late Archean Tumbiana Formation—an archive that has become an effective stratotype for ^{13}C-depleted Archean organic matter (Eigenbrode and Freeman, 2006; Hayes, 1994; Thomazo et al., 2009). These rocks are well suited for this analysis because they contain both kerogen and authigenic calcite cements preserved in stromatolitic laminations. We measured the carbonate cements that precipitated in the stromatolites at a finer texture-specific scale than has been done previously to look for any evidence of AOM, and combined traditional C and O isotope ratio measurements on the carbonate cements with clumped isotope analyses to evaluate the impacts of post-depositional processes on these materials. Finally we interpret the data in the context of a model of Archean carbonate chemistry, and discuss other potential metabolisms that might better explain the observations, such as the possibility that the ^{13}C-depleted Archean kerogens reflect an entirely different mode of biochemical carboxylation.

2. Geological background and methods

The Tumbiana Formation was deposited at 2721 ± 4 Ma during an interval of rifting and subsidence, and onlaps the Pilbara craton (Blake et al., 2004). It ranges in thickness from a few meters up to 320 m, and is lithologically diverse, consisting of conglomerates, shale, mudstones, siltstones, sandstones, breccias, basalts, tuff, and limestone (Thorne and Trendall, 2001). It is notably laterally variable containing many different facies that have been proposed to represent either lacustrine (Awramik and Buchheim, 2009; Buick, 1992; Coffey et al., 2013) or shallow marine settings (Sakurai et al., 2005; Thorne and Trendall, 2001); notably however, these facies all reflect shallow water paleoenvironments. This contrasts with typical methanotrophic environments both today and in Phanerozoic basins (typically slope/deep marine or within sedimentary pore fluids, Campbell et al., 2002; Campbell, 2006; Marlow et al., 2014; Michaelis et al., 2002) making the highly ^{13}C-depleted kerogens in the Tumbiana Formation intriguing and unique.

Samples were collected from outcrops of the Meentheena Member of the Tumbiana Formation at the Redmont/Knossos Area, Western Australia (22°02′44″S, 118°59′34″E) (Fig. 1). The Meentheena Member constitutes the uppermost sequence of the Tumbiana Formation, and is composed of a 30 to 50 m thick unit of interbedded carbonate (mainly limestone) and immature siliciclastic and volcaniclastic lithologies. The unit also contains spectacular occurrences of a diversity of well-preserved stromatolites (Awramik and Buchheim, 2009; Coffey et al., 2013; Flannery and Walter, 2012)—the lithologies targeted in this study. In the sampling locality, the exposure of the Meentheena Member outcrop is 11 m thick (Fig. S1). Here the Meentheena Member contains trough cross-stratified and wave-rippled sandstones and grainstones from coarse to very fine-grained, the latter of which become interbedded with stromatolites up section. Associated with mudcracks, these stromatolites developed in an intertidal environment that deepens to dominantly subtidal facies upsection (Sakurai et al., 2005).

Outcrop samples were cut into slabs and polished to reveal textures and provide fresh surfaces for analysis. Petrographic thin sections were made from book-matched surfaces of the slabs sampled for isotopic analysis, and imaged using light and electron microscopy. Scanning electron microscopy (SEM) and X-ray dispersive spectroscopy (EDS) were performed using a combined ZEISS 1550VP Field Emission SEM and Oxford INCA Energy 300 X-ray dispersive spectrometer at Caltech.

Powders for carbonate δ^{13}C and δ^{18}O isotopic analysis were collected using a micro-rotary drill with a 2 mm bit. Diverse textures (stromatolite with abundant grains, stromatolite with abundant cement, intercolumn sediment, across areas of differential recrystallization) were sampled in order to create a detailed cm-scale isotope ratio map of textures within these ancient microbial structures, and uncover the effects of diagenesis. Samples for organic δ^{13}C measurements were made on 5 to 10 g bulk stromatolite samples targeting organic-rich laminae, and excluding intercolumn sedimentary fill, cut and then powdered using a mortar and pestle.

Inorganic δ^{13}C and δ^{18}O isotopic measurements were performed at the University of Michigan Stable Isotope Laboratory. Carbonate sample powders were placed in stainless steel combustion boats and baked under vacuum at 200 °C to remove volatiles and water. Samples were then places in borosilicate reaction vessels and reacted at 77 °C with 4 drops of anhydrous phosphoric acid for 8 min in a Finnigan MAT Kiel IV preparation device coupled directly to the inlet of a Finnigan MAT 253 isotope ratio mass spectrometer. For 19 of the 50 samples, replicate splits were measured to assess accuracy and precision. Two NBS standards (NBS 18 and NBS 19) were run with the samples. Oxygen isotope ratio data were corrected for acid fractionation and source mixing by calibration to a best-fit regression line defined by standards. Analytical uncertainty is better than 0.1‰ for both carbon and oxygen isotopes. Data are reported in delta notation relative to VPDB standard.