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Spatially-resolved isotopic study of carbon trapped in ∼3.43 Ga Strelley Pool Formation stromatolites

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Abstract

The large isotopic fractionation of carbon associated with enzymatic carbon assimilation allows evidence for life's antiquity, and potentially the early operation of several extant metabolic pathways, to be derived from the stable carbon isotope record of sedimentary rocks. Earth's organic carbon isotope record extends to the Late Eoarchean-Early Paleoarchean: the age of the oldest known sedimentary rocks. However, complementary inorganic carbon reservoirs are poorly represented in the oldest units, and commonly reported bulk organic carbon isotope measurements do not capture the micro-scale isotopic heterogeneities that are increasingly reported from younger rocks. Here, we investigated the isotopic composition of the oldest paired occurrences of sedimentary carbonate and organic matter, which are preserved as dolomite and kerogen within textural biosignatures of the ∼3.43 Ga Strelley Pool Formation. We targeted least-altered carbonate phases *in situ* using microsampling techniques guided by non-destructive elemental mapping. Organic carbon isotope values were measured by spatially-resolved bulk analyses, and *in situ* using secondary ion mass spectrometry to target microscale domains of organic material trapped within inorganic carbon matrixes. Total observed fractionation of ^{13}C ranges from −29 to −45‰. Our data are consistent with studies of younger Archean rocks that host biogenic stromatolites and organic–inorganic carbon pairs showing greater fractionation than expected for Rubisco fixation alone. We conclude that organic matter was fixed and/or remobilized by at least one metabolism in addition to the CBB cycle, possibly by the Wood-Ljungdahl pathway or methanogenesis-methanotrophy, in a shallow-water marine environment during the Paleoarchean.
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1. INTRODUCTION

The stable carbon isotope values of organic matter and inorganic carbon provide a record of biological carbon assimilation extending to the early Archean (Fig. 1). The direction and magnitude of isotopic offset between the two carbon reservoirs reflects the integrated fractionations imparted by all biological processes contributing to organic matter burial, as well as any diagenetic processes, hydrothermal alteration and regional metamorphism altering the isotopic composition of carbon-bearing phases. In Precambrian rocks, average total fractionations are remarkably consistent (ε = ∼−26‰; Schidlowski, 1987) and are generally thought to reflect the early evolution and continuous operation of the Calvin-Benson-Bassham (CBB) cycle for carbon assimilation. In more recent studies, $\delta^{13}C_{org}$ values as low as −37‰ are interpreted in the context of the CBB cycle (e.g. Eigenbrode and Freeman, 2006).

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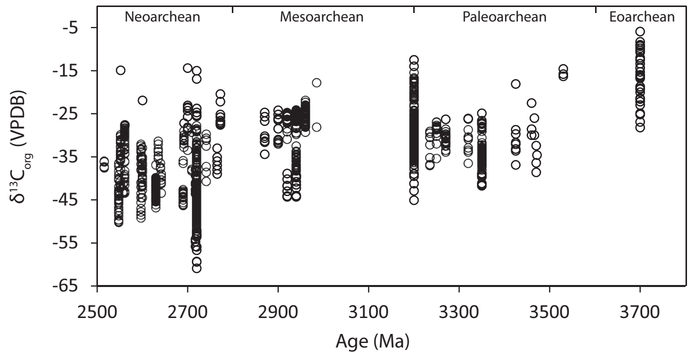

Fig. 1. Stable organic isotope values reported from Archean units, compiled from supplementary references and new data reported here.

However, greater fractionations are reported from some Precambrian units, most notably those deposited during the Neoarchean (Schidlowski, 1988). Highly ^{13}C-depleted Neoarchean values are widely interpreted as evidence for the activity of methane cycling microbial communities (Hayes, 1994). Archean methanogens and methanotrophs would have regulated atmospheric methane, possibly at comparatively high levels, which could have led to greenhouse warming that mitigated the reduced luminosity of the early sun (Pavlov et al., 2001). Methanogens may also have contributed to the rise of oxygen by producing CH_4 that underwent photolysis thereby allowing H_2 to escape to space preferentially (Catling et al., 2001). ^{13}C-depleted methane inclusions putatively preserved within hydrothermal precipitates of the Dresser Formation have been claimed as evidence for the evolution of methanogenesis prior to ~3.5 Ga (Ueno et al., 2006), but an abiological origin for these inclusions has also been proposed (Lollar and McCollom, 2006). Other circumstantial evidence for an early origin of methanotrophy includes the close phylogenetic relationship of archaeal methanotrophs and early-evolving methanogens (Hinrichs et al., 1999), and $\delta^{13}C_{org}$ values as low as -43‰ reported from Mesoarchean shale by Kiyokawa et al. (2006). Alternatively, these fractionations, which are greater than expected for fixation by D-ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) alone, could reflect CO_2 fixation via the Wood-Ljungdahl pathway (reductive acetyl-CoA pathway), which is generally considered capable of ^{13}C fractionations of −30 to −40‰ (Knoll and Canfield, 1998; Fischer et al., 2009). This pathway is employed by modern acetogenic bacteria in a process that culminates in ^{13}C fractionations of up to -69‰ in closed, laboratory-based systems (Freude and Blaser, 2016). Thus, it is conceivable the Wood-Ljungdhal pathway produced significant ^{13}C fractionations reported from Archean rocks. Regardless of the pathway(s) responsible, the timing of the evolution of metabolisms capable of greater fractionations than Rubisco remains poorly-known, primarily because paired occurrences of sedimentary carbonate and organic matter become increasingly rare in the early geological record. Here, we contribute new isotope data obtained from carbon sequestered in dolomite and organic matter associated with textural biosignatures in the ~3.43 Ga Strelley Pool Formation, the oldest known supracrustal carbonate sequence. Our dataset represents the oldest known paired occurrences of significant sedimentary carbonate and organic matter, and the oldest organic matter described from stromatolites. In order to select areas minimally-affected by isotopic shifts related to diagenesis, regional metamorphism and hydrothermal alteration, we targeted least-altered carbonate phases using microsampling techniques guided by non-destructive elemental mapping. Organic carbon isotope values were measured by bulk analyses and *in situ* by secondary ion mass spectrometry (SIMS).

2. GEOLOGICAL SETTING

The Strelley Pool Formation is an important stratigraphic marker within the early Archean Pilbara Supergroup, Western Australia. The Pilbara Supergroup was deposited during the Paleoarchean, contemporaneously with the development of a series of large granitoid bodies which now divide the Stelley Pool Formation (SPF) between 11 greenstone belts (Fig. 2). The SPF unconformably overlies volcanic and sedimentary rocks of the 3520–3427 Warrawoona Group and is unconformably overlain by ultramafic volcanic rocks of the 3350–3315 Ga Kelly Group (Hickman, 2008). It is locally up to 1 km thick and consists predominantly of sandstone, conglomerate, quartzite, volcaniclastic rocks and variably silicified sedimentary carbonate. The stratigraphy, sedimentology and trace element geochemistry suggest deposition occurred primarily within a shallow-water marine environment that was periodically influenced by hydrothermal fluids (Van Kranendonk et al., 2003; Hickman, 2008; Allwood et al., 2010). Biological activity during deposition of the unit is recorded by stromatolites (Allwood et al., 2006), biogenic isotopic fractionations (Wacey et al., 2010, 2011; Lepot et al., 2013) and microfossils (Sugitani et al., 2010, 2013; Wacey et al., 2011). Regional metamorphism in our study area was limited to greenschist facies (Hickman, 2008; Wacey, 2010).

3. METHODS

3.1. Fieldwork

Hand samples were collected from Strelley Pool Formation outcrop at Anchor Ridge in the North Pole Dome

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