

Marine organic matter cycling during the Ediacaran Shuram excursion

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ABSTRACT

Ediacaran (ca. 635–541 Ma) marine carbonates capture a global $\delta^{13}\text{C}$ carbon isotope excursion to extremely negative values ($\sim -12\%$)—known as the Shuram excursion (SE)—that cannot be explained by conventional mass balance scenarios. Furthermore, the carbon isotopic variation of bulk organic matter (OM) does not mirror that of carbonate through the excursion, suggesting that the OM reflects a mixture of different sources. To evaluate this hypothesis, we investigated thermally immature marine sedimentary rocks that record the SE from the Sultanate of Oman. Compound-specific carbon isotopic analyses of the extractable hydrocarbons reveal low $\delta^{13}\text{C}$ values of long-chain ($>C_{20}$) *n*-alkanes and mid-chain monomethyl alkanes as low as -40% . Such light signatures are rare in marine rocks of any age and provide evidence that the SE reflects a primary carbon cycle perturbation. The magnitude of the SE recorded in these organic phases is smaller than observed in carbonate and implies that the primary perturbation to dissolved inorganic carbon (DIC) was at least 5% – 7% , and more likely 7% – 12% , in magnitude when correcting for end-member source mixing. Due to isotopic differences in stratigraphic patterns of the different organic compounds, we propose that bulk organic carbon (both bitumen and kerogen) reflects source mixing between two distinct pools that previously masked the excursion in bulk $\delta^{13}\text{C}_{\text{org}}$ measurements. OM sources were derived both from autotrophs fixing ^{13}C -depleted DIC and from a less ^{13}C -depleted heterotrophic microbial biomass feeding on a marine OM pool sustained by petroleum expelled from older sedimentary OM. Expulsion of these sedimentary fluids also helps explain both the duration and magnitude of the SE.

INTRODUCTION

The enigmatic Shuram excursion (SE) is observed globally in late Neoproterozoic marine carbonates (Grotzinger et al., 2011). Data from bulk carbonates ($\delta^{13}\text{C}_{\text{carb}}$) reveal a large ($>12\%$) negative carbon isotope excursion in marine carbonates, which is not paralleled in the bulk organic carbon ($\delta^{13}\text{C}_{\text{org}}$) record (e.g., Fike et al., 2006; McFadden et al., 2008; Lee et al., 2013; Macdonald et al., 2013). The decoupling of carbonate and organic carbon isotope trends is unexpected if both are derived from the same source of dissolved inorganic carbon (DIC) (Rothman et al., 2003) and has led to competing hypotheses for the mechanism driving the SE: (1) oxidation of a large pool of dissolved organic carbon (DOC) in seawater (Rothman et al., 2003; Fike et al., 2006; McFadden et al., 2008); (2) multilayered ocean stratification (Ader et al., 2009); (3) sedimentary methane clathrate collapse (Bjerrum and Canfield, 2011); (4) a significant contribution of exogenous organic carbon sources in carbonates with low total organic carbon (TOC) content (Johnston et al., 2012); (5) post-depositional alteration of primary $\delta^{13}\text{C}_{\text{carb}}$ signatures (Derry, 2010; Knauth and Kennedy, 2009); (6) a bolide impact (Young, 2013); (7) amplification by authigenic carbonate precipitation (Macdonald et al., 2013; Schrag et al., 2013); and (8) mixed or multiple sources of organic carbon combined with diagenetic alteration of carbonates (Oehlert and Swart, 2014).

Prior organic carbon isotope records through the SE have focused on bulk organic matter (OM) derived from samples with low TOC content.

These records can be difficult to decipher because preserved sedimentary OM can contain a mixture of organic carbon inputs (e.g., Freeman et al., 1990; Johnston et al., 2012). Additional information can be provided by compound-specific carbon isotope analyses (CSIA). Because the carbon isotopic signature conferred on the hydrocarbon skeleton lipids during synthesis is retained on geological time scales (Hayes et al., 1990), CSIA provides a means of untangling OM records and interrogating more directly isotopic signatures of primary OM production.

Here we present detailed CSIA measurements of hydrocarbon fractions from marine organic-rich deep-water facies that span the SE in sedimentary strata in a drill core from the South Oman Salt Basin (Fig. 1; see the GSA Data Repository¹). A previous lipid biomarker study demonstrated that the OM in these strata is thermally well preserved, containing abundant extractable biomarkers (Fig. DR1 in the Data Repository) unaffected by contamination (Lee et al., 2013). Moderate to high organic carbon contents are found in rocks from the TM-6 core (range of 0.2–17 wt%; Lee et al., 2013), including in the stratigraphic intervals within and around the SE, indicating that OM production and burial in the ocean did not cease during the SE carbonate minimum.

RESULTS AND DISCUSSION

^{13}C -Depleted Compounds: Long-Chain Alkanes

Linear (*n*-alkanes) and mid-chain monomethyl alkanes (MMAs) constitute the two dominant resolvable series of compounds in the saturated hydrocarbon fractions. Long-chain *n*-alkanes ($>nC_{22}$) in sedimentary

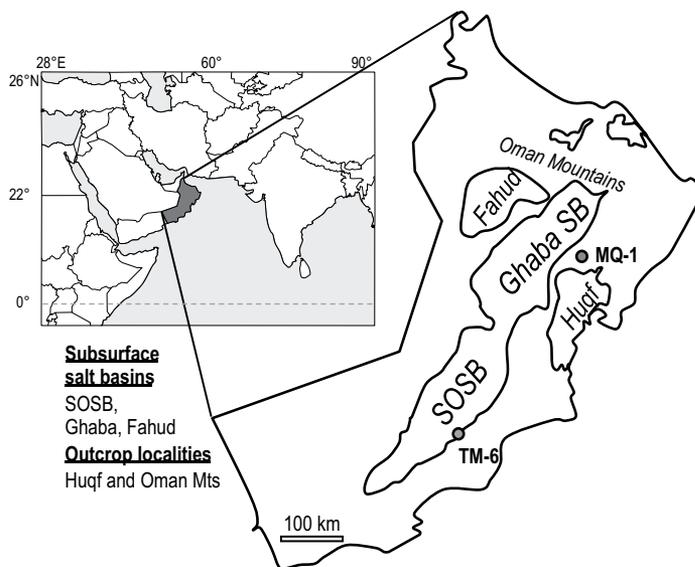


Figure 1. Map of Sultanate of Oman showing South Oman Salt Basin (SOSB) and location of TM-6 core on eastern flank and MQ-1 core from Fike et al. (2006). SB—salt basin.

¹GSA Data Repository item 2015367, supplemental information, is available online at www.geosociety.org/pubs/ft2015.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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marine OM can have mixed sources (i.e., from algae and bacteria), but the proportion of algal contributions is expected to be higher (Love et al., 2005). The biological precursor lipids of this particular series of MMAs (also known as X-peaks)—long-chain linear alkanes with a single methyl branch in the middle—have not been uniquely identified. However, they are thought to be bacterial products associated with benthic microbial mats (Love et al., 2008).

Long-chain (nC_{20} – nC_{28}) n -alkanes (Fig. 2C) and MMAs (C_{20} – C_{28}) (Fig. 2D) during the SE display a broad negative excursion in $\delta^{13}C$ spanning hundreds of meters of stratigraphy, with MMA values dropping over a range from -33‰ to -40‰ . $\delta^{13}C$ values of nC_{20} – nC_{28} n -alkanes range from $\sim -32\text{‰}$ to $< -38\text{‰}$ (Fig. 2C) and are similar to n -alkane values previously reported from South Oman (e.g., Höld et al., 1999), but much lower than values from other Lower Cambrian–Proterozoic strata (Fig. DR2). Although n -alkanes and MMAs are ^{13}C depleted (approaching values of -40‰), they are not sufficiently ^{13}C depleted to be substantially derived from methanotrophy (Birgel et al., 2008). The 5‰ – 7‰ excursion in individual hydrocarbons coincides stratigraphically with the -12‰ $\delta^{13}C_{carb}$ anomaly observed both in TM-6 and throughout Oman (Burns and Matter, 1993; Le Guerroué et al., 2006; Lee et al., 2013). The most ^{13}C -depleted values for n -alkanes and MMA series in TM-6, as for bulk organic carbon, are found stratigraphically higher than the most ^{13}C -depleted carbonate interval within the Shuram Formation (Fig. 2). This stratigraphic offset points to a two-end-member OM source mixing during the peak of the SE that explains the decoupling of organic and inorganic carbon isotopes and hints that the true magnitude of the excursion in marine DIC might be greater than 5‰ – 7‰ . Hence, these new

data confirm that the SE reflects, at least in part, a primary perturbation to the Neoproterozoic carbon cycle.

We also measured the isotopic composition of additional compounds with autotrophic sources, commonly derived from the phytol side chain of chlorophylls: the isoprenoids pristane (Pr) and phytane (Ph). $\delta^{13}C$ values for Pr and Ph during the SE average $-35.2\text{‰} \pm 0.05\text{‰}$ and $-35.3\text{‰} \pm 0.09\text{‰}$, respectively, and trend toward heavier $\delta^{13}C$ values with depth below the SE (Fig. 2E). These values are not as low as those observed in coeval n -alkanes and MMAs, but the degree of ^{13}C depletion is likely underestimated because these compounds were measured on a substantial “heavy” unresolved complex mixture (UCM) baseline (Fig. DR3) even after considerable efforts to cleanly isolate these compounds. We interpret these values as a mixture of ^{13}C -depleted Pr and Ph with ^{13}C -enriched UCMs given that UCMs are the most ^{13}C -enriched alkane components we observed. Thus, Pr and Ph must be more ^{13}C depleted than the measured -35‰ —perhaps several per mil lighter. Overall, the Pr and Ph data support a photoautotrophic input to OM during the SE that is more ^{13}C depleted than typically observed in marine sedimentary basins of any age.

^{13}C -Enriched Compounds: UCM and Branched and Polycyclic Hydrocarbons

UCMs are common features in gas chromatograms of extractable hydrocarbon constituents of Proterozoic sedimentary OM (e.g., Pawlowska et al., 2013). Proterozoic UCMs display a substantial rise in the baseline at high molecular weights forming a “humped” feature (Fig. DR3) of hundreds of largely unidentified branched and polycyclic hydrocarbons

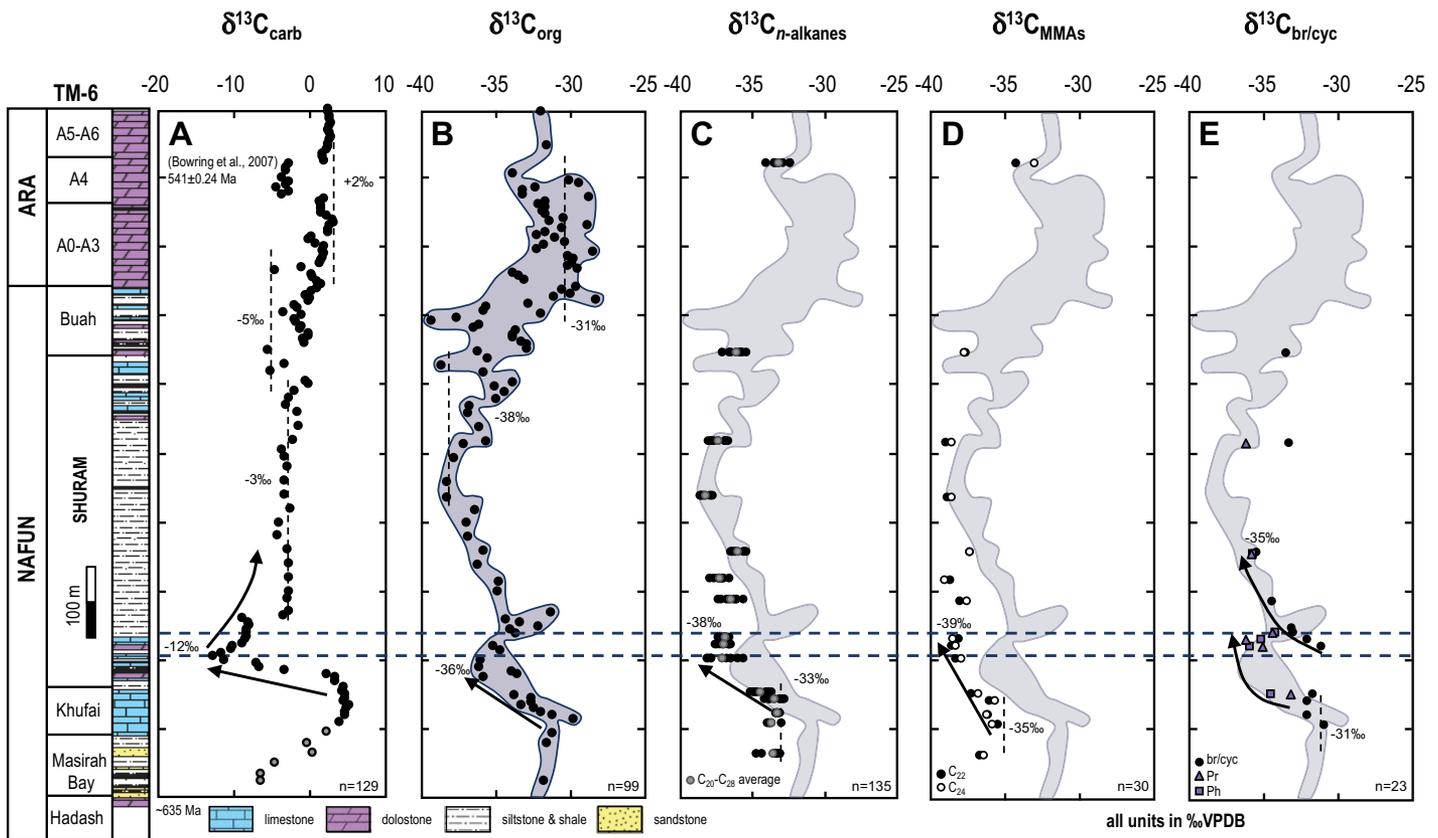


Figure 2. Carbon isotope ($\delta^{13}C$) trends through core TM-6 (Lee et al., 2013). **A:** Marine carbonates (note the gray points in Masirah Bay Formation are likely influenced by diagenetic processes). **B:** Bulk organic carbon. **C:** C_{20} – C_{28} n -alkanes, with gray circles indicating average $\delta^{13}C$. **D:** C_{22} (filled circles) and C_{24} (open circles) mid-chain monomethyl alkanes (MMAs). **E:** Bulk branched and polycyclic hydrocarbons (br/cyc); purple triangles and squares are $\delta^{13}C$ pristane (Pr) and phytane (Ph), respectively. Blue dashed lines and black arrows highlight nadir and immediate recovery of the excursion in $\delta^{13}C_{carb}$ and response of organic phases (B–E). Blue shaded region shows profile of bulk $\delta^{13}C_{org}$. All values have units in per mil Vienna Peedee belemnite (‰ VPDB).

(br/cyc) derived from structural diagenetic alteration. UCMs are also seen in lower relative abundance in alkane chromatograms from Phanerozoic rocks with $\delta^{13}\text{C}$ isotopic values typically ^{13}C enriched relative to *n*-alkanes and other well-resolved alkane series. Importantly, this bulk branched and polycyclic fraction shows a different stratigraphic $\delta^{13}\text{C}$ trend than the other alkane series and is consistently the most ^{13}C -enriched hydrocarbon component and dominated compositionally by the UCM. Khufai carbonates, which precede the SE, record a small $\sim 1\%$ positive excursion in $\delta^{13}\text{C}_{\text{br/cyc}}$ isotopes, followed by a 4% negative excursion reaching -35% above the Shuram minimum in $\delta^{13}\text{C}_{\text{carb}}$ with recovery to -33% (Fig. 2E). Notably the UCM is greatest in relative abundance in strata around the carbonate isotopic minimum and coincident with the largest offset between $\delta^{13}\text{C}_{\text{MMAs}}$ and $\delta^{13}\text{C}_{\text{br/cyc}}$ (lightest and heaviest organic carbon) of 8.4% .

OM versus Carbonates as Archives of Carbon Cycle Change

Sedimentary carbonates provide a view of the global carbon cycle through the lens of local environmental and biological processes (e.g., carbonate precipitation mechanisms and mineralogy; Husson et al., 2015)—processes that can impact carbonate isotopic compositions and enhance (or mask) the changes in the isotopic composition of DIC. For the SE, some have argued that the pattern observed in $\delta^{13}\text{C}_{\text{carb}}$ reflects secular changes in diagenetic processes rather than primary seawater perturbations to carbon cycle mass balance (Knauth and Kennedy, 2009; Derry, 2010; Schrag et al., 2013). While a range of observations suggest that diagenetic processes did not alone account for the trends observed in $\delta^{13}\text{C}_{\text{carb}}$ (Bergmann et al., 2011; Lee et al., 2013; Husson et al., 2015), the absolute magnitude of the perturbation to DIC remains uncertain. If the SE in core TM-6 is interpreted as a perfect reflection of seawater, the $\delta^{13}\text{C}_{\text{carb}}$ data imply a DIC excursion of 17% (Fig. 2A).

Organic carbon phases also provide a measure of the isotopic composition of DIC, filtered by microbial metabolisms and ecology. CSIA values for alkanes through the SE record at least an $\sim 5\%$ – 7% isotopic excursion that coincides with the main carbonate isotopic excursion. This shift is much smaller than that observed in carbonates, but nevertheless implies that the SE records a carbon cycle perturbation of significant size. Consequently, the isotopic change in DIC through the SE must have been $\geq 5\%$, and perhaps much greater because source mixing appears to have buffered the magnitude of the ^{13}C depletion in the hydrocarbon fractions.

Isotope mass balance approaches to deconvolve the different sources, allowing for small 1% – 2% isotopic fractionations of saturated hydrocarbons from bulk $\delta^{13}\text{C}_{\text{org}}$ from South Oman rocks (e.g., Grosjean et al., 2009), suggest that the true magnitude of the negative SE for autotrophic organic carbon is 7% – 12% offset from the baseline pre-Shuram value of -30% for bulk OM (Fig. DR4). Using a 10% – 50% contribution of a heavy end-member composition of -30% at the nadir in $\delta^{13}\text{C}_{\text{carb}}$ and a bulk $\delta^{13}\text{C}_{\text{org}}$ value of -36% gives an estimate of the light end-member OM in the range of -37% to -42% . Although this solution is not unique, it does imply that the primary carbon isotopic shift associated with the SE is significant and greater than the observed 5% – 7% for individual alkanes and 6% for bulk organic carbon. An estimated 7% – 12% magnitude in excursion for the autotrophic organic carbon end member is still substantially lower than the 17% excursion in $\delta^{13}\text{C}_{\text{carb}}$ over the SE, requiring other contributing factors to explain the overall carbonate excursion.

Finally, because similar C_{org} isotopic profiles are seen both for rock bitumen and kerogen for core TM-6 (Lee et al., 2013), the carbon isotope decoupling between these phases and the compound-specific trends is not due to local oil staining of the rocks but involves a two-end-member endogenous biomass input to host sediments at the time of deposition.

A Possible Mechanism

The SE punctuates a long interval of high $\delta^{13}\text{C}_{\text{carb}}$ values widely observed in Ediacaran strata (e.g., Husson et al., 2015, and references therein). A reasonable interpretation of these high $\delta^{13}\text{C}_{\text{carb}}$ values is sus-

tained high relative rates of organic carbon burial in sedimentary basins globally, the duration of which is not well constrained but could be tens of millions of years. This is long enough to build up a substantial pool of ^{13}C -enriched organic-rich source rocks buried and matured to the stage of oil generation in multiple basins around the world (Fig. DR4), the influence of which may have been magnified by the large number of passive-margin basins formed during the breakup of the supercontinent Rodinia (Bradley, 2008).

Enhanced organic carbon burial in newly formed Ediacaran basins was previously proposed (Knoll et al., 1986), and estimates of the global crustal organic carbon pool suggest that this reached modern levels for the first time (Des Marais et al., 1992). Thus we hypothesize that the SE reflects an interval of enhanced mass transfer of these hydrocarbon-rich fluids from sedimentary reservoirs to the fluid Earth—a large and dynamic suite of geophysical processes in sedimentary basins (Huuse et al., 2010). The source of the fluids need not reflect a single or specific source, though there could have been multiple global sources with possible tectonic drivers, such as the Pan-African orogenies, playing an important role in synchronizing catagenesis and expulsion of petroleum in different basins through the duration of the SE minimum. Furthermore, the middle Ediacaran is thought to be a time of increased tectonic activity (Halverson et al., 2007; McKenzie et al., 2014), and enhanced weathering could have increased the oxidant supply needed to drive the oxidation of OM under this subsurface seepage scenario.

This hypothesis explains both the source mixing observed in sedimentary OM in Oman as well as the phase shift between carbonate and organic isotope trends. In this scenario, a heterotrophic marine OM pool, partially decoupled from surface primary production, significantly fueled by seepage of relatively ^{13}C -enriched OM from the subsurface, would have produced ^{13}C -depleted DIC through OM oxidation (and a source for the carbonate excursion) while buffering bulk $\delta^{13}\text{C}_{\text{org}}$ through the peak and immediate recovery of the SE. As hydrocarbon-rich fluid fluxes dropped, this buffering capacity waned and was exhausted through the mid-Shuram Formation, reflected in the recoupling between the isotopes of carbonate and OM. Additional support for this scenario comes from $\delta^{13}\text{C}_{\text{org}}$ values of -39% in the Buah Formation that match those of the upper Doushantuo Formation (IV), South China (McFadden et al., 2008), at the level where carbonate-OM isotope coupling resumes. The seepage of petroleum from subsurface source rocks as a major source flux of marine carbon expelled over hundreds of thousands to millions of years has been proposed previously to explain significant perturbations to $\delta^{13}\text{C}_{\text{carb}}$ isotope records for the Paleocene-Eocene transition (Kroeger and Funnell, 2012). The protracted release of a vast pool of reduced carbon into the ocean in the middle Ediacaran may have produced a redox barrier that suppressed the diversification and expansion of Metazoa until the late Ediacaran. If the hypothesis that the SE was driven by enhanced carbon fluxes from sedimentary basins is correct, it suggests that this mechanism was capable of driving substantial carbon cycle perturbations in Earth's past.

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