The stratigraphic expression of a large negative carbon isotope excursion from the Ediacaran Johnnie Formation, Death Valley

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ABSTRACT
The Rainstorm Member of the Ediacaran Johnnie Formation of the southern Basin and Range, US, records a large negative excursion in carbon isotope ratios of carbonate strata (δ13CVPDB > −6‰). The character of the excursion raises fundamental questions about whether this isotopic pattern is accurately capturing the time-series behavior of marine dissolved inorganic carbon (DIC) or is a product of diagenesis. To explore this issue, we examined the expression of this isotopic excursion within the Johnnie oolite, a ~2 m thick marker bed, which records the highest rate of change in δ13C. Sedimentologically, the oolite is thought to be time-transgressive; if the isotopic excursion reflects time-series behavior of the carbon cycle, its expression in the oolite across the basin should systematically align the sections according to their slight diachroneity. Detailed carbon and oxygen isotopic stratigraphy of the oolite at seven different locations indicates the magnitude of the excursion at the base of the oolite is spatially variable such that after a palinspastic reconstruction the sections align along a systematic north to south gradient in the isotopic data. The oolite preserved in the Old Dad Mountains, the most southerly section measured, is an outlier to this trend (and the most difficult to ordinate accurately in the reconstruction), showing the largest isotopic range between the onset of carbonate deposition and top of the oolite. Several hypotheses are congruent with these data, but the sum of observations is best explained by a scenario wherein the oolite is time-transgressive and deposited in a north to south manner throughout the onset of the isotopic excursion. If correct, this implies that the stratigraphic δ13C pattern reflects time series behavior of marine DIC.

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1. Introduction
Carbonate-bearing sedimentary successions of Neoproterozoic age record extreme negative excursions in δ13C (and sometimes δ18O) that are distinct from Phanerozoic excursions and difficult to explain because of their unusual geological and geochemical attributes (Calver, 2000; Fike et al., 2006; Jiang et al., 2007; Kaufman et al., 2007; Melezhik et al., 2005). The most spectacular of these events is known as the Shuram Excursion (SE) because of its discovery in the Shuram Formation of the Nafun Group, Sultanate of Oman (Burns and Matter, 1993; Le Guerroue et al., 2006b; McCarron, 2000). This chemostratigraphic pattern is found in at least four depositional basins separated at the time of deposition Oman (Burns and Matter, 1993; Fike et al., 2006), South Australia (Calver, 2000), South China (Jiang et al., 2007; McFadden et al., 2008), Western USA (Corsetti and Kaufman, 2003; Kaufman et al., 2007; Verdel et al., 2011), but possibly many more (Siberia (Melezhik et al., 2009; Pokrovskii et al., 2006), Namibia (Ries et al., 2009; Saylor et al., 1998), Scandinavia (Melezhik et al., 2005, 2008), and Scotland (Prave et al., 2009)). As yet, these excursions lack direct geochronological constraints, but they invite global correlation because they sit, broadly, in middle Ediacaran age strata, between the ~630 Ma Marinoan glaciation (Condon et al., 2005) and the Precambrian-Cambrian boundary at 542 Ma (Bowring et al., 2007; Grotzinger et al., 1995). The excursions are all characterized by δ13CVPDB values in carbonate-bearing minerals below −6‰. Such light values are considered extreme for a primary marine signal because they exist outside the solution space for carbon isotope mass balance models wherein the isotopic composition of the inputs are often set to presumed mantle values (e.g. Kump, 1991). These rocks do not show a corresponding excursion in δ13Corg and tend to be organic lean (Calver, 2000; Fike et al., 2006; McFadden et al., 2008; Rothman et al., 2003). Many chemostratigraphic sections also show co-varying δ13C and δ18O across both dolomite and calcite lithologies (Burns and Matter, 1993; Calver, 2000; Derry, 2010; Knauss and Kennedy, 2009). There is some evidence that these excursions coincide with a drop to more negative δ34S values (Fike et al., 2006; Kaufman et al., 2007; McFadden et al., 2008). Successions recording the excursions are commonly composed of mixed...
carbonate and silicilastic sediments. Purple siltstones and pink carbonates (including calcitic pink ooid grainstones) exist in multiple sections globally, and have a distinctive sequence stratigraphic and lithologic similarity (Calver, 2000; Kaufman et al., 2007; Le Guerroué et al., 2006a; McCarron, 2000; Melezhik et al., 2009). While robust geochronologic constraints do not exist on the duration and timing of these excursions, they generally span hundreds of meters of stratigraphic thickness (Calver, 2000; Fike et al., 2006; Melezhik et al., 2005, 2009). Estimates of the length of time represented by the stratigraphy are on the order of 5–50 million years, far greater than the presumed residence time of carbon in Ediacaran seawater (Fike et al., 2006; Jiang et al., 2007; Le Guerroué, 2010; Le Guerroué et al., 2006b), but see Rothman et al. (2003).

Special interest exists in understanding the nature of these isotopic excursions because of possible connections to a state change in the reduction–oxidation potential of the fluid Earth (Canfield et al., 2007; Fike et al., 2006; Halverson et al., 2005, 2010; Kaufman et al., 2007; Le Guerroué et al., 2006a; McCarron, 2000; Melezhik et al., 2009). These hypotheses that explain a large, long-lived negative excursion in marine dissolved inorganic carbon (DIC) and produce no excursion in coevally deposited organic carbon invoke dynamic models of the carbon cycle wherein the carbon budget includes the demise (via remineralization) of large masses (or proportions) of organic carbon, putatively in the form of dissolved organic carbon (DOC) in seawater (Fike et al., 2006; Kaufman et al., 2007; McFadden et al., 2008; Rothman et al., 2003). These hypotheses have been criticized from perceived incompatibilities with oxidant chemistry required to remineralize such a large DOC pool (Bristow et al., 2005, 2009). Estimates of the length of time represented by the stratigraphy are on the order of 5–50 million years, far greater than the presumed residence time of carbon in Ediacaran seawater (Fike et al., 2006; Jiang et al., 2007; Le Guerroué, 2010; Le Guerroué et al., 2006b), but see Rothman et al. (2003).

In addition to this criticism, several details of the chemostratigraphic pattern have raised questions about whether or not this pattern accurately reflects a time-series history of marine DIC. Because carbonate-bearing minerals are often subject to recrystallization and re-equilibration with pore fluids after deposition, the covarying relationship between δ13C and δ18O, and the lack of a similar excursion in organic phases has fueled hypotheses that the isotopic excursions have a root diagenetic cause (Bristow and Kennedy, 2008).

We sought to test if the negative δ13C excursion recorded in the oolite demonstrates a slight diachroneity between seven locations in the southern Basin and Range province due to time-transgressive deposition (Fig. 2). If the isotopic composition of the oolite shows clear and systematic basin-scale stratigraphic trends once palinspastically reconstructed, the most parsimonious explanation is that the isotopic signal was a feature present during the formation and deposition of the oolite and thus accurately reflects a negative excursion in marine DIC. No systematic variability across the basin would suggest either synchronous deposition or wholesale diagenetic alteration of any primary signal. Alternatively, clear isotopic variation that is predicted by independent observations of the preservation of petrographic textures would imply that diagenetic processes were responsible for the carbon isotope pattern that defines the excursion.

2. Geologic setting

The preserved Neoproterozoic stratigraphy in the Death Valley Region in the southwestern United States (Fig. 1) overlies gneissic (1.7 Ga) and granitic (1.4 Ga) basement (Labotka et al., 1980), and begins with the Pahrump Group, which includes the Crystal Spring Formation, the Beck Spring Formation and Kingston Peak Formation (Stewart, 1970). The Neoproterozoic record also includes the Noonday Formation, Johnnie Formation, Stirling Formation and the lower Wood Canyon Formation (Fig. 1) (Stewart, 1970). Robust geochronologic constraints on Pahrump Group strata are rare; diabase dikes within the Crystal Spring Formation yield U/Pb ages of 1087 ± 3 Ma and 1069 ± 3 Ma (Heaman and Grotzinger, 1992). The Kingston Peak Formation includes several diamicrite horizons that have been correlated with Neoproterozoic glacial deposits constrained elsewhere to between 723 Ma and 580 Ma (Corsetti and Kaufman, 2003; Corsetti et al., 2007; Prave, 1999). The Noonday
Formation, predominately dolomite in composition, includes, at its base, unusual sedimentary features characteristic of Marinoan cap carbonates. It has been correlated to other Marinoan sections using litho- and chemostratigraphy (Corsetti and Grotzinger, 2005; Corsetti and Kaufman, 2003; Petterson et al., 2011); if these correlations are correct, the Noonday is ca. 630 Ma in age. An upper age constraint on the Johnnie Formation comes from paleontological observations. Ediacaran fossils have been documented in the Stirling Formation, and the lowermost Wood Canyon Formation includes the Precambrian-Cambrian boundary, with an implied age of ca. 542 Ma (Bowring et al., 2007; Condon et al., 2005; Corsetti and Hagadorn, 2000; Hagadorn et al., 2000; Hagadorn and Waggoner, 2000). Within these constraints, the Johnnie Formation was deposited between 630 Ma and 542 Ma, and probably sits in the middle Ediacaran, deposited between 580 and 550 Ma (Kaufman et al., 2007; Pruss et al., 2008).

This Neoproterozoic through early Cambrian sedimentary sequence records a transition from continental rifting associated with the breakup of Rodinia to the development of a passive margin on western Laurentia (Bond et al., 1985; Levy and Christie-Blick, 1991; Stewart, 1972). The timing of active rifting is still debated but strong differences in stratigraphic thickness exist in both the Kingston Peak Formation and Johnnie Formation suggesting brief periods of rifting and unequal subsidence, although the possibility remains that the observed incision of the upper Johnnie Formation was glacially driven or part of a marine canyon system (Abolins, 1999; Clapham and Corsetti, 2005; Fedo and Cooper, 2001; Stewart, 1972, 1983).

2.1. Stratigraphy of the Rainstorm Member

The Johnnie Formation is a mixed siliciclastic and carbonate succession composed of shales, siltstones, quartzites, conglomerates, limestones and dolostones (Stewart, 1970), and has been divided into seven sequences (Summa, 1993). The Johnnie Formation disconformably overlies the Noonday in most locations but extends beyond the outcrop extent of the Noonday and overlies the Kingston Peak Formation in the Silurian Hills and Precambrian basement rocks in the Old Dad Mountains (Summa, 1993). The Rainstorm Member, the focus of this study, comprises the uppermost Johnnie Formation, includes the siltstones of sequence 5, all of sequence 6 and part of sequence 7 (Fig. 1) (Summa, 1993). This study’s reference section of the Rainstorm Member is located in the northern Nahop Range and consists of purple siltstones above and below a ~2 m thick, ochre-colored, dolomitic oolite. This oolite is colloquially known as the “Johnnie oolite” because it is an important regional stratigraphic marker (Figs. 1 and 3) (Stewart, 1970; Summa, 1993). Overlying the oolite, the Rainstorm Member continues with orange dolomitic sandstones and pink limestones that include ooid and intraclast grainstones (Summa, 1993). In the southern Nahop Range, these beds are capped by grey limestone beds containing aragonite crystal fan pseudomorphs (now calcite).
which are overlain by more siltstones (Figs. 3 and 4) (Pruss et al., 2008; Summa, 1993). In several locations, and observable along strike, conglomeratic beds associated with an erosive surface originating from high in the Rainstorm Member incise deeply into the underlying strata, and can locally contain blocks \( \sim 15 \) m in size (Clapham and Corsetti, 2005). This conglomerate unit, thought to be associated with continental rifting or glaciation, is overlain by more siltstones before the boundary with the Stirling Formation (Fig. 1) (Abolins, 1999; Clapham and Corsetti, 2005; Summa, 1993).

3. Methods

3.1. Field work and sample preparation

To examine the sequence stratigraphic nature of the excursion captured by the Rainstorm Member Johnnie oolite, multiple sections were measured and sampled in seven locations across the Death Valley region mountain ranges during the fall of 2008 and the spring and summer of 2010 (Fig. 2) (GPS coordinates in Table S1). These locations were selected to examine spatial patterns across the preserved sedimentary basin. They also record a large range of post-depositional diagenetic and structural modifications. The Panamint Mountains, for example, were buried deeper and reached much higher peak temperatures compared to the other ranges used in this study (Labotka et al., 1980, 2000; Prave, 2000). It was evident in the field that some sections show abundant outcrop-scale faulting of the oolite; these include the Resting Spring Range and the southern Nopah Range (Trower and Grotzinger, 2010). This range of preservation between different locations, allows for some testing of diagenetic hypotheses.

The oolite was sampled at very high stratigraphic resolution with samples taken every 10 cm or less. To test the extent of local variability within the carbon and oxygen isotopic systems, two separate oolite sections were sampled \( \sim 50 \) m apart at each location. Carbonate beds found above the oolite and below the Johnnie/Stirling Quartzite contact were also sampled and described where present. Hand samples were sectioned with a rock saw to provide unweathered surfaces. Powders for \( \delta^{13}C \) and \( \delta^{18}O \) analyses were sampled using a micro-rotary drill with a 2 mm bit targeting regions with well-preserved ooids. Matrix cements were included in the samples but effort was made to avoid fractures and secondary veinings. Representative thin sections were made from each section to observe patterns of diagenesis and compare the preservation of carbonate textures between the different locations (Fig. 4).

3.2. Mass spectrometry

Carbon and oxygen measurements were made at the University of Michigan Stable Isotope Laboratory. Each sample powder was heated to 200 °C to remove volatile contaminants and water. 20–30 \( \mu \)g of sample was reacted in a common anhydrous H\(_3\)PO\(_4\) acid bath held at 77 ± 1 °C for 12 min. The reaction occurred in a Finnigan MAT Kiel IV preparation device that directly introduced the evolved CO\(_2\) sample into a Finnigan MAT 253 gas source mass spectrometer. Isotopic measurements were calibrated against NBS 18 and NBS 19. Accuracy and precision, measured by multiple analyses of known standards, are better than ±0.1‰. Isotope ratios for both carbon and oxygen are reported by reference to Vienna Pee Dee Belemnite (VPDB).
4. Results

4.1. Northern Spring Mountains (NS)

The northern Spring Mountains section is the northernmost section sampled in this study. The Noonday Formation–Johnnie Formation contact is not exposed but the documented thickness of the Johnnie Formation at this locale is 354 m (Summa, 1993). The thickness from the oolite to the contact with the Stirling Formation is ∼ 80 m (Fig. 5) (Summa, 1993). Much of the section above the oolite is covered, but the 1.5 m oolite is well exposed. A thin (∼ 20 cm) pink ooid grainstone bed is located ∼ 27 m above the oolite. Conglomerate beds also appear ∼ 16 m below the base of the Stirling at this location (Fig. 5) (Summa, 1993). Two sections of the oolite were sampled approximately 50 m apart. Both sections record declining δ13C values, from −2.9‰ and −3.2‰ at the base to −4.9‰ and −4.9‰ at the top of the oolite (Fig. 6). There is good agreement in both the pattern of decline and absolute magnitude of the two sections (Fig. 6). In the northern Spring Mountains, the Johnnie oolite is highly fractured compared to other sections and the ooids were not as well preserved in all samples. Nonetheless the δ13C values show small first differences and a steady decline with stratigraphic height (Figs. 4b, c and 6).

4.2. Resting Spring Range (RS)

The Johnnie Formation is also incomplete in the Resting Spring Range and the thickness of the Rainstorm Member is variable. In the section measured for this study, the thickness from the oolite to the contact with the Stirling Formation is ∼ 50 m (Fig. 5). In the measured section, the oolite is encountered twice, likely due to duplication by a thrust fault. The upper oolite may also be structurally thickened (4 m versus −1.3 m) and the decline in δ13C occurs over a slightly smaller range (Fig. 6). In the two sections sampled from the lower exposure of oolite, δ13C values begin at −2.9‰ and −2.9‰ and drop to values of −5.3‰ and −4.3‰ over 1.3 m. δ13C begins at −4.7‰ in the second oolite and more gradually drops to −5.9‰ at the top (Fig. 6). The Resting Spring section also has a very thin (10 cm) bed of pink micritic limestone near the base of the Stirling contact (∼ 30 m above the upper exposure of oolite). This bed records a δ13C value of −8.0‰ (Fig. 5). In the Resting Spring Range, the Rainstorm Member is very similar in both lithology and thickness to the northern Spring Mountain section.

4.3. Johnson Canyon, Panamint Mountains (JC)

The Johnson Canyon section is located in the Panamint Mountains in Death Valley but is very similar lithologically to Rainstorm Member exposures in the southern Nopah Range. The thickness from the oolite to the contact with the Stirling Formation is ∼ 160 m and is the thickest of this study (Verdel, 2009; Verdel et al., 2011). The base of the oolite has δ13C values of −3.8‰, which decline to −5.6‰ at the top of the oolite. The pink limestones are thicker in Johnson Canyon than in the Spring Mountains and Resting Spring Range and they sit closer to the oolite. Overlying the oolite are 5 m of siltstones and 6.5 m of pink carbonates showing declining δ13C values ranging from −8.6‰ to −11.0‰. Rare carbonate beds in ∼ 150 m of siltstone and sandstone below the Stirling contact are also isotopically depleted but become less depleted up section from −11.4‰ to −8.2‰ (Verdel, 2009).

4.4. Southern Nopah Range (SN)

The Johnnie Formation is well exposed throughout the southern Nopah Range. In the section measured for this study, the thickness from the oolite to the Stirling contact is ∼ 100 m and includes...
coarse conglomeratic beds. There is evidence that the oolite sampled and measured for this study was structurally thickened from post-deposition thrusting because it is \(\sim 4.4\) m thick versus average oolite thicknesses of about 2 m in other sections in the southern Nopah Range (Summa, 1993; Trower and Grotzinger, 2010). There is also less dramatic change in \(\delta^{13}C\) from the bottom to the top of the oolite. The base of the oolite records \(\delta^{13}C_{VPDB}\) values of \(-4.0\)‰ and decrease to \(-4.9\)‰ at the top (Fig. 5). There are approximately 10 m of siltstone and orange carbonate-cemented sandstone between the oolite and pink limestones (Fig. 5). The sequence of pink limestones is thick (\(~20\) m) and includes intraclast and ooid grainstones with a variable number of grey limestone beds (\(~5–6\) ) that contain crystal fan pseudomorphs (Figs. 4 and 5). The carbon isotopes in the pink limestone unit are more depleted in \(\delta^{13}C_{VPDB}\) (\(-11.2\)‰) than in Johnson Canyon and become slightly less depleted in \(\delta^{13}C_{VPDB}\) by the top of the pink limestones (\(-9.6\)‰) (Fig. 1).

4.5. Northern Mesquite Mountains (NM)

The upper Johnnie Formation in the northern Mesquite Mountains is thinner when compared to the Johnson Canyon and southern Nopah Range sections (\(~65\) m from the oolite to the Stirling contact), but carbonate lithologies comprise more of the preserved section (Fig. 5) (Summa, 1993). The two sections of the oolite begin at \(-4.8\)‰ and \(-4.5\)‰ and become more \(\delta^{13}C_{VPDB}\)-depleted up section, falling to \(-6.0\)‰ and \(-5.5\)‰ (Fig. 6). The two sections agree well in excursion shape and magnitude for the first two meters. One section is thicker and \(\delta^{13}C_{VPDB}\) continues to decline to \(-6.0\)‰ (Fig. 6). The limestone beds 13 m above the oolite are thickly bedded pink ooid and intraclast grainstones with occasional small red chert nodules. \(\delta^{13}C_{VPDB}\) analyses from these beds range
from $-10.9\%$ to $-9.9\%$. The limestones are approximately 45 m thick and disappear from the section close to the Stirling contact (Fig. 5) (Summa, 1993).

### 4.6. Salt Spring Hills (SS)

The Salt Spring Hills section of the Johnnie Formation is overall much thinner than the sections directly to the north, $\sim 250$ m versus 600 m in the southern Nopah Range and 385 m in the northern Mesquite Mountains (Summa, 1993). The oolite $\delta^{13}C_{VPDB}$ composition in the Salt Spring Hills begins at $-5.5\%$ and $-5.8\%$ in the two sections sampled and falls to $-6.0\%$ and $-6.9\%$ at the top of the oolite (Fig. 6). The isotopic composition of the section that is more $^{13}C$-depleted at the top ($-6.9\%$) shows more variability throughout the last meter of the oolite, and is also half a meter thicker (Fig. 6). There are no beds of pure carbonate above the oolite before the contact with the Stirling Quartzite but the section includes 12 m of siltstones directly above the oolite and $\sim 25$ m of dolomite-cemented sandstone beds (Summa, 1993).

### 4.7. Old Dad Mountains (OD)

The southern-most section measured in this study is the most lithologically distinct. The entire section is only 165 m thick, even thinner than the Salt Spring Hills section (Summa, 1993). The Johnnie sits unconformably on gneissic basement; the older Pahrump Group strata are absent (Stewart, 1970). When mapping the lower sequences of the Johnnie, Summa (1993) noted that the first sequence is completely absent whereas the second sequence is thickened locally and dominantly carbonate, unlike other Death Valley sections. The Johnnie oolite at this section is extremely variable in thickness and can be locally surrounded by non-oolitic thickly laminated carbonates below and stromatolitic carbonates above (Summa, 1993). Additionally, the isotopic range in $^{13}C$ is the largest among any section. The two sections sampled are $\sim 30$ m from each other and yet the first oolite sampled (0.6 m thick) sits on top of siltstones and below a massive stromatolitic dolostone (1.6 m thick) and the other oolite sampled (0.35 m) is underlain by non-oolitic thickly laminated carbonates interbedded with siltstones (1.7 m thick) and overlain by siltstones (Fig. 5). The $\delta^{13}C_{VPDB}$ at the base of the 0.6 m oolite is $-1.8\%$ and the top of the oolite is $-3.0\%$. The massive carbonate directly overlying the oolite shows a continued decline from $-3.5\%$ to $-5.1\%$. A 20 cm carbonate bed $\sim 1$ m below the oolite was analyzed and $\delta^{13}C_{VPDB}$ falls from $-1.3\%$ to $-1.6\%$ over 15 cm. The $\delta^{13}C_{VPDB}$ of the laminated carbonates at the base of the second section begins at $-1.4\%$ and falls to $-2.8\%$. The overlying oolite shows a continued decline from $-3.2\%$ to $-4.0\%$ at the top of the oolite (Fig. 6). There are $65$ m of shale and siltstones preserved above the oolite, a pattern that is similar to the Rains- storm in the northern Spring Mountains and Resting Spring Range (Fig. 5). Directly below the base of the Stirling Formation, there are two massive cross-stratified carbonate grainstone beds (0.5 m thick and 2 m thick, respectively) with shale in between the beds (Fig. 5). The $\delta^{13}C_{VPDB}$ composition from the one sample analyzed from the lower bed is $-9.2\%$. The three samples from the upper bed with increasing stratigraphic height are $-7.5\%$, $-8.4\%$ and $-10.0\%$.

### 5. Discussion

#### 5.1. Petrographic and isotopic comparison across all sections

The depleted $\delta^{13}C$ and $\delta^{18}O$ data could be explained by either a primary marine signal, later diagenetic recrystallization and resetting, or a combination of the two. The preservation of primary textures can be an important indicator of the degree of diagenetic alteration and can begin to differentiate between these two mechanisms. Corsetti et al. (2006) completed a detailed analysis of the petrography and paragenesis of the Johnnie oolite using plane polarized light and cathodoluminescence. They found abundant evidence that the ooids underwent dolomitization very early in their history and that this transformation preserved much of the fine details of the original ooid fabrics and early marine cements. Some sections within their survey had evidence for later vadose zone cements and meteoric cements. These findings are consistent with our petrographic observations. Examples of ooids with well-preserved radial textures, individual cortices and detached cortices that were not destroyed by the surrounding cementation can be found in Fig. 4a and b. Some sections also include a poorly preserved end member characterized by micritized ooids and abundant fractures indicating further diagenetic modifications (Fig. 4c). The pink limestones overlying the oolite also show exceptionally preserved fabrics and record even more extreme $^{13}C$ and $^{18}O$ values. These textures include pseudomorphs of primary aragonite crystal fans that likely underwent stabilization to calcite very early in their history as well as extremely well preserved radial ooids (Fig. 4d) (Sandberg, 1983).

Each section is characterized by declining $\delta^{13}C$ compositions with stratigraphic height and small first differences between samples. In contrast, the $\delta^{18}O$ values are highly variable with stratigraphic height and show no clear trend. The different character of the carbon and oxygen datasets suggest the oxygen isotopic compositions have been diagenetically reset while the possibility exists that the majority of the carbon isotopic compositions have not been reset. Pruss et al. (2008) microsampled the crystal fan pseudomorphs in the pink limestones and found the different phases (fans versus early marine cements) can be isotopically indistinguishable. Thus across several orders of magnitude in scale, the $^{13}C$ data reveal a similar consistent pattern, despite being recorded in a wide range of fabrics that were differentially susceptible to fluid flow and diagene

When aligned using the base of the oolite as a datum, the range in $\delta^{13}C$ of the different locations is striking (Fig. 7a). The $\delta^{13}C_{VPDB}$ at the base of the oolite ranges from $-1.8\%$ in the Old Dad Mountains to $-5.8\%$ in the Salt Spring Hills. The base of the oolite in the Old Dad Mountains is $-1\%$ heavier than the northern Spring Mountains and Resting Spring Range. The northern Spring Mountains and Resting Spring Range oolites are $-1\%$ heavier at the base than in Johnson Canyon, the southern Nopah Range and northern Mesquite Mountains. Finally, the northern Mesquite Mountains and southern Spring Range are $-1.5\%$ heavier than the base of the Salt Spring Hills oolite (Fig. 6). The top of the oolite records a range of values from $-4.0\%$ in the Old Dads to $-6.9\%$ in the Salt Spring Hills (Fig. 7a).

If the sections are aligned by their basal isotopic composition instead of by the stratigraphic datum and allowed to be mildly stretched or compressed (on the y-axis) to account for variable sedimentation rates through time, a general curve of changing isotopic composition emerges (Fig. 7b). Each section overlaps in $^{13}C$ values with other sections. Rare single data points deviate from this curve in a few locations including the top of the southern Nopah Range section and the thicker of the two Salt Spring Hills sections indicating the isotopic record preserved in the thicker oolites could be complicated by structural folding and faulting (Fig. 7b).

Finally, despite clear evidence for fabric-retentive and fabric-destructive recrystallization in these rocks, $^{13}C$ and $^{18}O$ are not strongly correlated over the thickness of the oolite. This is distinct from several previous trends documented for large-magnitude negative $^{13}C$ excursions elsewhere, and does not readily conform to the proposed diageneric models (Derry, 2010; Knauth and Kennedy, 2009). The six sections measured in the Salt Spring Hills, Johnson Canyon and northern Mesquite Mountains sections all define loose clusters in C–O space. In the Old Dad Mountains some of the most
5.2. Isotopic results in the context of palinspastic reconstruction

Two periods of intense deformation in the Death Valley region have resulted in isolated exposures of the Johnnie Formation. Mesozoic crustal shortening and thin-skinned deformation resulted in several major thrust sequences that were oriented loosely parallel to the Laurentian margin, running north to south. Subsequent Cenozoic extension of the Basin and Range was oriented east-west and smeared out many of the pre-existing structures (Snow and Wernicke, 2000; Wernicke et al., 1988).

To examine spatial patterns in the nature of the excursion observed in the Johnnie oolite, we used a palinspastic reconstruction of the central Basin and Range, constructed by Snow and Wernicke (2000) to un-do the Cenozoic extension. Their reconstruction relies on the reassembly of thrust fault exposures between the existing mountain ranges, regional facies and isopach correlations in the Death Valley region. Under this hypothesis, the key observation for reconstructing the Neoproterozoic sections rests on correlation of the Wheeler Pass thrust system in the Spring Mountains, the Chicago Pass thrust system in the northern Nopah Range and the Panamint thrust system in the Panamint Mountains (Snow and Wernicke, 2000). This restores the Neoproterozoic sections to a thin north-south trending band that completely lies within the Wheeler Pass thrust sheet. From north to south the sections are as follows: northern Spring Mountain (NS), Resting Spring Range (RS), the Panamint Mountains’ Johnson Canyon (JC), southern Nopah Range (SN), northern Mesquite Mountains (NM), the Salt Spring Hills (SS) and Old Dad Mountains (OD) (Fig. 8). The Los Vegas Valley shear zone complicates the placement of the Old Dad Mountains within the reconstruction (Snow and Wernicke, 2000). The Johnson Canyon section and the southern Nopah Range (SN) section restore to almost directly east-west of each other, an arrangement hypothesized by Stewart (1983) on the basis of offsets in both lithostratigraphy and isopach trends along the Furnace Creek fault system. In the reconstruction, the east-west distances preserved are small (∼25 km) while there remains a large north-south distance between sections (∼200 km) (Snow and Wernicke, 2000).

When the isotopic results are overlayed on the palinspastic reconstruction they exhibit a north to south trend within the Wheeler Pass thrust sheet with the exception of the Old Dad Mountains (Fig. 8). The basal composition of the oolite in the northernmost section is the least depleted while the southern Salt Spring Hills section is the most depleted. This pattern is consistent with the interpretation that the oolite is time transgressive and is recording a change in the isotopic composition of marine DIC. The carbonates preserved in the Old Dad Mountains would have been deposited first, while the northern Spring Mountains and Resting Spring Range would follow subsequently. The transgressing ooid shoals would reach the Salt Spring Hills last. Cessation of oolite deposition appears to follow a similar time-transgressive trend (Fig. 9).
Fig. 8. (a) Current locations of the seven sampled sections of the Johnnie showing faults with significant displacement. The locations are the same as in Fig. 2 but ordinated with numbers indicating the degree of δ¹³C depletion at the base of the oolite relative to the other locations, with one being the heaviest. Major Cenozoic faults are shown and labeled as Garlock Fault (GF), Panamint Valley Fault Zone (PVFZ), Owens Valley Fault (OVF), Hunter Mountain Fault (HMF) North Death Valley—Funeral Creek Fault (NDV—FCF), and South Death Valley Fault (SDVF). (b) Palinspastic reconstruction accounting for Cenozoic extension aligns all locations in a North to South pattern within the Wheeler Pass thrust sheet. Reconstruction using relationships from Snow and Wernicke (2000) and Wernicke et al. (1988).

Fig. 9. Chronostratigraphic diagram where isotopic composition is traded for relative time on the y-axis. The seven locations are ordered the same as in Fig. 8, with the heaviest δ¹³C compositions at the base of the oolite on the left side of the diagram and the more depleted compositions on the right side of the diagram. The isotopic range in the overlying pink limestones is also shown for the locations where the observations exist. The isotopic scale for the pink limestones reflects whether the sections preserve the climbing limb of the excursion, the recovery or both. Data from this study (Kaufman et al., 2007; Verdel et al., 2011). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)
The sedimentology of the ooids (grain size and cross-stratification) reveals similar degrees of agitation and wave energy; it is very likely that the oolite was deposited under similar paleoenvironments and water depths, and records the isotopic characteristics of a well-mixed water column and is not recording a gradient in the water column.

The north to south isotopic trend revealed by this analysis is interesting because it suggests different distal versus proximal trends and paleoshoreline geometries than previous interpretations (Stewart, 1970). The shoreline to shelf direction has been interpreted as oriented (modern day) east to west with the paleoshoreline running north to south based on isopach maps, grain size trends and carbonate abundance within the overlying siliciclastic formations (i.e. Stirling Quartzite, Wood Canyon Formation and Zabriskie Quartzite) (Stewart, 1970). The isotopic pattern on the other hand suggests the shelf direction to be north-south and the paleoshoreline to be more east-west. This interpretation matches the craton margin position (trending NE-SW) proposed by Fedo and Cooper (2001).

Additional sedimentologic evidence for this north-south distal-proximal interpretation includes isopach maps of the Johnnie Formation. Isopach data indicates both the Johnnie Formation and the thickness of the oolite to Stirling contact is thinnest in the southernmost sections—the northern Mesquite Mountains (~385 m thick Johnnie, ~70 m thick oolite to Stirling), the Salt Spring Hills (~250 m, ~45 m), the Silurian Hills (~115 m, ~7 m), and the Old Dad Mountains (~165 m, ~45 m) (Summa, 1993). The thickness and facies of the overlying pink limestones also suggest the northern sections are the most distal. In those sections the pink limestones are thin (10–20 cm thick) and micritic (Fig. 5) (Summa, 1993). They are thickest in our proposed near shore sections—Johnson Canyon, southern Nopah Range and northern Mesquite Mountains where they sit between 5 and 15 m above the oolite and are between 10 and 45 m thick (Fig. 5) (Summa, 1993). In these sections the pink limestones are mainly ooid and intraclast grainstones interpreted to represent storm deposits. In the Salt Spring Hills section, suggested by the isotopic data to be the most proximal, the pink limestone beds are missing entirely and are replaced by high-energy dolomite cemented sandstone beds (Fig. 5). The unusual sedimentary structures, limestone composition and color (with precipitation of authigenic minerals) indicate that the pink limestone beds were probably deposited during an interval of maximum flooding following the transgression associated with the oolite deposition.

5.3. The Old Dad Mountains section is an outlier

The isotopic data for the Old Dad Mountains is not in line with the north-south trend seen across the other sections but its placement in the palinspastic reconstruction is the least constrained because of the Las Vegas Valley shear zone. Both the isotopic data and sedimentology from the Old Dads suggest that the sediments might have been deposited in a tectonically isolated sub-basin (Figs. 5 and 6). The oolite in the Old Dads appears to be the first deposited as its basal isotopic composition is the least depleted in δ13C (Figs. 5 and 6). The isotopic composition of the carbonates just below the Stirling contact suggest they were deposited at the same time or slightly earlier than the pink limestone facies in other locations even though there exists a substantial amount of intervening stratigraphy above the oolite in the Old Dad Mountains (~60 m, in other sections this package is 5–30 m) (Fig. 9).

Sedimentologically, the Old Dad Mountains are anomalous. The Johnnie Formation overlies crystalline quartzose gneissic basement, which is rare for the lower contact (Summa, 1993). Additionally Summa (1993) identified two sequences within the lower Johnnie that also indicate the Old Dad Mountains might have been subject to unique basin dynamics. The lower most sequence of the Johnnie Formation is present in more northerly sections, thins to the east and is absent in the Salt Spring Hills and Old Dad Mountains. The second sequence is also spatially variable and in the Old Dad Mountains it is one of the thickest exposures, and composed of pure carbonate unlike other sections suggesting that if a sub-basin existed this is when it became active (Summa, 1993). The character of the Rainstorm Member is also unusual as the oolite is surrounded by thinly laminated carbonates and stromatolitic to massive carbonates as opposed to siltstone and shale lithologies (Fig. 5) (Summa, 1993). The sedimentology and isotopic character of the Old Dad Mountains suggests very different sedimentation styles and rates compared to other sections supporting a model of an isolated sub-basin.

5.4. Could this sedimentary isotopic pattern represent a diagenetic signal?

There are two leading diagenetic hypotheses to explain large negative carbon isotopic excursions preserved in Neoproterozoic strata; but each invokes a set of diagenetic processes that are very different in their nature and respective timing (Derry, 2010; Knauth and Kennedy, 2009). Oxygen isotope ratio data and observation of carbonate textures in these samples reveals clear evidence of post-depositional alteration. We can know with certainty that the chemistry of these rocks has been affected by recrystallization and re-equilibration with diagenetic fluids. However, petrographically these samples are well-preserved, suggesting any such recrystallization occurred very early. The isotopic pattern within the Johnnie oolite and overlying pink limestones is neither uniform nor random across space, which is a challenging pattern to relate to known diagenetic processes. The spatial pattern observed can be used to test the robustness of these hypotheses for the origin of this carbon isotope excursion.

It is possible that our observed decline in the isotopic composition of the oolite and overlying carbonates could be produced by mixing with a plume of meteoric fluids moving through the oolite and overlying carbonates from nearshore sediments to more distal deposits (e.g. Knauth and Kennedy, 2009). In that scenario, one would expect the nearshore environments and the more permeable sediments to be the most isotopically altered. The oolite is the most permeable carbonate-bearing lithology in these sections. The Johnnie oolite presents the main fluid flow path for altering fluids, should have experienced higher water to rock ratios, and would therefore be predicted to have the most altered (13C-depleted) isotopic composition. There is no doubt that the oolite was host to a variety of post depositional fluids as evidenced by the variety of intergran cement preservatives within the oolite (Corsetti et al., 2006). The overlying pink limestones, which include early-cemented crystal fans, should be less altered (more 13C- and 18O-enriched) than the oolite. The documented pattern shows exactly the opposite. Also according to this hypothesis (Knauth and Kennedy, 2009), the Old Dad Mountains section should also reflect its cratonward location (more proximal to the source of altering fluids) and look similar to the Salt Spring Hills. Instead the oolite in the Old Dad Mountains has an isotopic composition that is the heaviest of all locations.

The burial diagenesis model proposed by Derry (2010), in which the isotopic composition reflects oxidation of organic matter from anomalously organic-rich Neoproterozoic rocks during deep burial, is difficult to rigorously assess in the Death Valley succession. These rocks present a challenge to look cleanly through the different episodes of deformation experienced by each of the different mountain ranges. However, there are a few observations in our data that bear on this hypothesis. As with other Ediacaran successions that record large negative excursions including the Shuram
and Wonoka Formations, the rocks in the Rainstorm member of the Johnnie are organic lean today (Calver, 2000; Fike et al., 2006; Kaufman et al., 2007), and probably lacked a rich basinal source of hydrocarbons to provide high fCO2, low δ13C altering pore fluids. In addition, our results demonstrate that the isotopic signal preserved in the Johnnie oolite is systematic with stratigraphic height and systematically variable across the reconstructed Johnnie basin. Under this hypothesis we would expect the most depletion in the down dip (north) direction; again, this is opposite of the observed chemostatigraphic pattern. We should also expect that, as stated above, the alteration would have followed expected patterns of permeability and water to rock ratio; these are not observed. That in mind, it is possible that a clean diageneric signal has been obscured by multiple episodes of diageneis. Still, the observation remains that these sections record a recognizable and repeatable signal across mountain ranges with different burial histories. This is consistent with the chemostatigraphic pattern being present in these rocks prior to Mesozoic time.

The systematic carbon isotopic variability observed in the Johnnie oolite does not appear to be well explained by existing diageneric hypotheses. Within the oolite in each section the δ13C composition becomes systematically heavier with stratigraphic height with small differences between adjacent samples. Across multiple sections tens of meters apart, the isotopic pattern is repeatable. Finally, a general north to south pattern of decreasing δ13C is apparent across the Johnnie sedimentary basin. This isotopic pattern is consistent across orders of magnitude in length scale and lends support for the hypothesis that it captures elements of a primary isotopic signal. We therefore tentatively regard these carbon isotopic data as reflecting a trend in the isotopic composition of marine DIC.

6. Conclusions

Aspects of the geology and geochemistry of large magnitude negative δ13C anomalies expose fundamental issues in our ability to explain and understand chemostatigraphic patterns using uniform hypotheses. The results from this high-resolution study of the Johnnie oolite, which records the onset of one such negative excursion, add additional geologic constraints for future models. We demonstrate a systematic and reproducible stratigraphic pattern in the carbon isotope ratios of Rainstorm Member carbonates that aligns stratigraphic sections along a north to south gradient in a palinspastic reconstruction. These isotopic data fit the interpretation that deposition of the oolite was time transgressive. They also agree well with surrounding sedimentology and stratigraphy that suggest the northerly sections were more distal and the southerly sections were more proximal. The spatial pattern recorded in carbon isotope ratios is better explained by hypotheses whereby the oolite records time-series behavior of marine DIC, than hypotheses in which the δ13C pattern is a result of post-depositional alteration. Though absolute resolution of the problem remains currently out of reach, these results contribute to the growing list of geological observations that must be met by any satisfactory explanation of this large negative carbon isotope excursion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.precamres.2011.03.014.

References


