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Carbon Isotope Variations Associated with a Middle Ordovician Karstic Unconformity

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CARBON ISOTOPE VARIATIONS ASSOCIATED WITH A

MIDDLE ORDOVICIAN KARSTIC UNCONFORMITY

By

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Bachelor of Science in Geology and Geophysics Missouri University of Science and Technology 2012

A thesis submitted in partial fulfillment of the requirements for the

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ABSTRACT

Carbon Isotope Variations Associated with a Middle Ordovician Karstic Unconformity

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Large negative carbon isotope (δ^{13} C) excursions have been documented from late Neoproterozoic-Paleozoic successions. These δ^{13} C excursions have been widely used for regional and global stratigraphic correlation, particularly in strata with limited paleontological and radiometric age controls. Recent studies, however, argued that some negative δ^{13} C excursions from stratigraphic record may have been resulted from meteoric/burial diagenesis, which commonly shifts both carbon and oxygen isotopes toward lower values. Testing the diagenetic origin of $\delta^{13}C$ excursions in stratigraphic successions without independent stratigraphic framework has been difficult because it evolves into circular arguments about stratigraphic completeness vs. diagenetic imprints. To address this issue, carbon and oxygen isotope analyses was conducted on the biostratigraphically controlled Middle Ordovician Antelope Valley Limestone Formation in the Arrow Canyon Range, Nevada, USA to document (1) the C-O isotope patterns of meter-scale cycles leading up to a well-known karstic unconformity and (2) isotope variability among carbonate lithologies and facies. The data are then compared with coeval isotope records regionally and globally to identify the maximum and minimum degree of isotope variations associated with meteoric/burial diageneses below a karstic

unconformity. The results may have implications for interpreting the origin of some negative δ^{13} C excursions, particularly those in the late Neoproterozoic.

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INTRODUCTION

Carbon isotope values of marine carbonates $(\delta^{13}C_{\text{carb}})$ presumably record the isotope signature of seawater. In the modern ocean, the primary seawater $\delta^{13}C$ signature is close to 0‰. Because the ocean is well mixed and has a large dissolved inorganic carbon (DIC) reservoir (~3.8 x 10¹⁹ g carbon), any major departure in $\delta^{13}C_{\text{carb}}$ (exceeding 2‰ differences) from the average seawater signature require substantial changes in the global carbon cycle and oceanography. Large $\delta^{13}C_{\text{carb}}$ excursions from marine carbonate rocks are thus considered to be recording major paleoceanographic events and can be used for global stratigraphic correlation (e.g., Knoll et al., 1986; Brasier et al., 1994; Kaufman and Knoll, 1995; Saltzman et al., 1998; 2005; Halverson et al., 2005). However, because carbonate rocks and their associated isotope signatures can be modified by meteoric and burial diagenesis, to what degree the $\delta^{13}C_{\text{carb}}$ values from ancient rocks record seawater signature has been debated (e.g., Swart , 2008; Derry, 2010; Knauth and Kennedy, 2009; Swart and Kennedy, 2012; Oehlert and Swart, 2014).

The primary vs. secondary origin of $\delta^{13}C_{\text{carb}}$ excursions in late Neoproterozoic successions is a typical example of debate. Numerous studies have documented large negative δ^{13} C shifts with a nadir down to \leq -5‰ (Kaufman and Knoll, 1995; Hoffman et al., 1998; Jacobsen and Kaufman, 1999; Halverson et al., 2005; Fike et al., 2006; Jiang et al., 2007; Grotzinger et al., 2011). These negative $\delta^{13}C_{\text{carb}}$ anomalies are difficult to interpret using traditional carbon cycle models because their minimum $\delta^{13}C_{\rm carb}$ values are even lower than the average $\delta^{13}C_{\rm carb}$ values of crustal rocks ($\approx -5\%$) and atmospheric $CO₂$ ($\approx -6\%$). Two interpretations have dominated in the last three decades.

In one interpretation, $\delta^{13}C_{\text{carb}}$ values obtained from Neoproterozoic carbonate-rich successions record a primary seawater signature because carbon is a major elemental component in carbonates, but a minor component in diagenetic fluids (e.g., Knoll et al., 1986; Kaufman et al., 1991; Kaufman and Knoll, 1995; Halverson et al., 2005; Jacobsen et al., 1999; Grotzinger et al., 2011). Under this assumption, $\delta^{13}C_{\text{carb}}$ anomalies can be a very useful chemostratigraphic tool for global stratigraphic correlation, particularly in strata with limited paleontological and radiometric age controls. They are also important evidence for substantial climate and oceanographic changes during the late Neoproterozoic, at the dawn of animal life (e.g., Hoffman et al., 1998; Halverson et al., 2005; Fike et al., 2006; Johnston et al., 2012).

The other interpretation emphasizes diagenetic overprints on Neoproterozic δ^{13} C_{carb} anomalies when carbonates interact with meteoric and formation fluids (e.g., Knauth and Kennedy, 2009; Swart and Kennedy, 2012). If carbonates were in contact with meteoric/formation fluids long enough and the fluid/rock ratios were high, rockfluid interaction would significantly modify the isotope values of carbonate rocks. Therefore, using δ^{13} C anomalies for stratigraphic correlation and paleoceanographic interpretation would be problematic, particularly in strata with uncertain age constrains (e.g., Melezhik et al., 2001; Swart, 2008; Knauth and Kennedy, 2009; Derry, 2010; Swart and Kennedy, 2012; Oehlert and Swart, 2014).

Evaluating the diagenetic overprint on Neoproterozoic $\delta^{13}C_{\text{carb}}$ anomalies is difficult because of the inability to establish an independent chronostratigraphic framework in which $\delta^{13}C_{\text{carb}}$ values of coeval units can be confidently compared. This is

largely due to the lack of reliable paleontological data and radiometric ages in most Precambrian successions.

In a recent study, Knauth and Kennedy (2009) compiled the $\delta^{18}O$ and $\delta^{13}C_{\text{carb}}$ values of Neoproterozoic–Phanerozoic carbonates and found apparent co-varying $\delta^{13}C$ $δ^{18}$ O trend. They interpreted that $δ^{13}C_{\text{carb}}$ values falling on the co-varying $δ^{13}C-δ^{18}O$ trend and those $\delta^{13}C_{\text{carb}}$ scatters with more negative $\delta^{18}O$ values, were most likely formed during carbonate lithification and subsequent diagenetic alterations. Based on this, they concluded that the appearance of large negative $\delta^{13}C_{\text{carb}}$ anomalies in the late Neoproterozoic was possibly due to colonization of primitive land plants for the first time in Earth history. Other studies also demonstrated that the co-varying $\delta^{13}C-\delta^{18}O$ trend from carbonate rocks is an indicator of diagenetic alteration (e.g., Kaufman and Knoll, 1995; Derry, 2010). In contrast, an earlier study (Allan and Matthews, 1982) indicated that δ^{13} C– δ^{18} O patterns vary along meteorically influenced surfaces. These uncertainties compel for more case studies across well-known karstic unconformities to better understand the isotope patterns associated with meteoric (and subsequent burial) diagenesis during sea-level fall events.

In this study, there will be an integrated sequence and chemostratigraphic study along the karstic unconformity below the Eureka Quartzite in the Mid-Late Ordovician section of the southern Great Basin (Figs. 1 and 2). By measuring carbon and oxygen isotopes of cyclic carbonate rocks below the Eureka Quartzite, this research will focus on (1) the temporal $\delta^{13}C - \delta^{18}O$ pattern across a stratigraphic interval leading up to a karstic unconformity, (2) the $\delta^{13}C - \delta^{18}O$ change within meter-scale carbonate cycles, and (3) the δ^{13} C_{carb} - δ^{18} O variations among different carbonate lithologies and facies. The overall

negative $\delta^{13}C_{\text{carb}}$ values and diagenetic $\delta^{13}C - \delta^{18}O$ patterns below a karstic unconformity provide a case study for the diagenetic overprints on carbon and oxygen isotopes and may lend insights for understanding the origin of late Neoproterozoic negative $\delta^{13}C_{\text{carb}}$ excursions.

STRATIGRAPHY, SAMPLING, AND ANALYTICAL METHODS

The Eureka Quartzite, at the middle-late Ordovician transition, is the most prominent siliciclastic unit within a more than 5000-m-thick, carbonate-dominated Paleozoic succession in the Great Basin (Langenheim et al., 1962; Fig. 3). The base of the Eureka Quartzite is a well-known karstic unconformity that may have had meteoric fluid influence tens to more than a hundred meter below the unconformity (e.g., Cooper and Keller, 2001). It serves as an ideal stratigraphic interval to understand meteoric diagenetic influences on carbon and oxygen isotope values. Preliminary isotope analyses by Kosmidis (2009) indicated that negative $\delta^{13}C_{\text{carb}}$ values below the Eureka Quartzite are common, but $\delta^{13}C_{\text{carb}} - \delta^{18}O$ patterns are quite variable among different sections.

This study focuses on a 184-m-thick interval below the Eureka Quartzite in the northern Arrow Canyon Range (ACR) (Fig. 2). Stratigraphically, the study interval covers the upper part of the Pognip Group Unit E (Ope) and the entire Unit F (Opf) (Langenheim et al., 1962) (Fig. 3). Langenheim (1962) divided the Pogonip into 6 units, Opa-Opf. The Ope unit (0–55.5 meters) is almost entirely limestone with fossil sponges, brachiopods, echinoderms, trilobites, gastropods, and oncoids distributed throughout (Langenheim et al., 1962). The Opf unit (55.5–184 meters) has a gradational contact with Ope at the base, and unconformably underlies the Eureka quartzite. The lower part of Opf is limestone and the upper part, near the quartzite, is dolomite (Langenheim et al., 1962). This unit has fossil gastropods, bivalves, brachiopods, *Receptaculites* sp., and oncoids, which distinguishes from the Ope. *Receptaculites* sp. may correlate strata between Arrow Canyon and Ibex Hills (Langenheim et al., 1962; Stricker and Carozzi,

1973). The Opf of Langenheim (1962) in the Arrow Canyon Range is roughly correlatable with the Pogonip unit 9 in the Nopah Range (Cooper and Keller, 2001).

The age of Ope and Opf has not been precisely determined in this region, but according to available biostratigraphy, these units should be of late White Rockian or late Darriwilian-earliest Sandbian (Saltzman et al., 2005a, 2005b), near the Middle-Late Ordovician transition (Fig. 3).The Eureka Quartzite (EQ) has an estimated age of late Chatfieldian through late Edenian (Druschke et al., 2009). Existing carbon isotope studies from a few global successions show near zero or slightly negative (>-2‰) $\delta^{13}C_{\text{carb}}$ values across this time interval, but no significant negative δ^{13} C excursion has been documented (Fig. 4; Saltzman et al., 2005a, 2005b; Ainsaar et al., 2010; Munnecke et al., 2010; Albanesi et al., 2013). Recently negative $\delta^{13}C_{\text{carb}}$ values down to -5‰ are reported from strata below the Eureka Quartzite in central Nevada (Kosmidis, 2009; Edwards and Saltzman, 2014).

The karstic unconformity below the Eureka Quartzite in the region represents a prominent subaerial exposure/erosional surface (e.g., Cooper and Keller, 2001). The δ^{13} C_{carb} values below the Eureka Quartzite, if they have been altered by meteoric diagenesis, are expected to cover different stratigraphic thickness depending on the permeability of ancient carbonate facies and fluid penetration. The $\delta^{13}C_{\text{carb}}$ - $\delta^{18}O$ patterns may vary, depending on the depth of the paleo-water table, intensiveness of water-rock interaction, and surface soil formation (Fig. 5; Allan and Matthews, 1982). Isotope values may vary among carbonate components such as micritic matrix, bioclasts and other particles including oncoids and ooids due to their differential resistance to diagenetic modification. Burial diagenetic fractures, cements, and structurally formed

veins would have distinguishable $\delta^{13}C_{\text{carb}}$ and $\delta^{18}O$ values. In addition, meter-scale cycles may show isotope variations, but the range of C-O isotope variations in individual cycles may be smaller than the isotope variations immediately below the karstic unconformity. Temporally, $\delta^{13}C_{\text{carb}}$ values should be most negative close to the unconformity and gradually change to the middle Ordovician background values away from the unconformity.

To test these hypotheses, samples were collected within a cyclo-stratigraphic framework to document the general $\delta^{13}C_{\rm carb}$ - $\delta^{18}O$ pattern of Ope and Opf units, leading up to the base of the Eureka Quartzite. Detailed samples were collected temporally across two meter-scale cycles to test the amount of $\delta^{13}C_{\text{carb}}$ - $\delta^{18}O$ variations within individual cycles. In addition, large rock slabs that contain bioclasts, oncoids, and/or later diagenetic cements or veins have been collected to test the isotope variations among carbonate components. A total of 188 samples were analyzed for $\delta^{13}C_{\text{carb}}$ and $\delta^{18}O$ values.

Hand samples were cut perpendicular to bedding in the University of Nevada Las Vegas Rock Preparatory Laboratory. Sixteen of those samples were sent to Quality Thin Sections to be polished and thin sectioned for petrographic study of diagenetic sequence.

For isotope analyses, carbonate powders (10–15 mg) were drilled from cleaned slabs. About 50–200 µg of sample powders were reacted with orthophosphorous acid for ten minutes at 70 °C in the Kiel IV Carbonate Device to generate purified $CO₂$, which was transferred to the dual-inlet Finnigan Delta V Plus Mass Spectrometer for carbon and oxygen isotope analysis. Analytical reproducibility was better than 0.1‰ for both $\delta^{13}C_{\rm carb}$ and δ^{18} O values, as monitored by NBS-19 and an internal standard. The isotope analyses

and sample preparation were conducted at the Las Vegas Isotope Science laboratory (LVIS) at University of Nevada-Las Vegas.

FACIES AND FACIES ASSOCIATIONS

Ten lithofacies are identified from the 184-m-thick section of the Antelope Valley Limestone Formation. These include (1) Thick-massive oncolitic-oolitic-bioclastic grainstone/packstone, (2) Oncolitic-bioclastic packstone with mudstone/lime mudstone lenses/drapes, (3) Bioclastic-oncolitic wackestone with mudstone/lime mudstone lenses, (4) Interbedded mudstone/lime mudstone with packstone interbeds, (5) Bioclastic lime mudstone/mudstone, (6) Oolitic-peloidal grainstone, (7) Intraclastic-bioclastic grainstonepackstone, (8) Bioclastic-peloidal wackestone, (9) Dolomitic lime mudstone with dissolution cavities, and (10) Microcrystalline dolostone. Their major features including constituents, bedding, and sedimentary structures are summarized in Table 1. The depositional model of these facies is delineated in Fig. 6 and some of their field/petrographic features are provided in Figures 7-10.

These facies are grouped into four facies associations according to their depositional environments including oncolitic-oolitic sand shoal, shallow lagoon, shallow subtidal, and tidal flat facies associations (Fig. 6A). The depositional environments of the measured section (Fig. 7) temporally changed from a rimmed carbonate shelf with a shoal complex at the shelf margin (0-82 m) to a shallow lagoon environment (83-113 m), and to open shelf peritidal (shallow subtidal and tidal flat) environments in the upper part (114-176 m). The measured section records an overall shallowing-upward sequence with facies prograding toward the west. In addition to the unconformity at the base of the Eureka Quartzite, three stratigraphic discontinuities characterized by abrupt facies change

are identified at 113 m, 137 m, and 172 m; their regional extension and significance requires further investigation (Fig. 7).

3.1 Oncolitic-oolitic sand shoal facies association

The sand shoal facies association occurs in the lower part of the measured section (0–82 m). It consists of three lithofacies (Table 1): thick-massive oncolitic-ooliticbioclastic grainstone/packstone (Facies 1), oncolitic-bioclastic packstone with mudstone/lime mudstone lenses/drapes (Facies 2), and bioclastic-oncolitic wackestone with mudstone/lime mudstone lenses (Facies 3). The grainstones-packstones are commonly 0.5–2 m thick. Oncoids vary from 5%–50% abundance and their sizes range from 0.5 cm to 2 cm (e.g., Figs. 8A). The remaining particles are ooids and bioclasts (Fig. 10A and B), which vary in abundance both laterally and vertically. *Receptaculites* sp. is found in varying abundance in this facies, but mostly in the upper part after 72 meters of the section. Some grainstone beds have erosional bases with 1–2 cm minor relief and occasionally, higher erosional relief (up to 5–10 cm) and cross bedding are observed.

In outcrop, oncolitic-bioclastic packstone with mudstone/lime mudstone lenses/drapes (Facies 2) looks similar to Facies 1 and the contact between these two facies are transitional. The most characteristic feature of this facies is the presence of thin (< 3 cm) lime mudstone/mudstone lenses and drapes (e.g., Fig. 8B). The lime mudstone/mudstone is laterally discontinuous and pinches out within decimeter distance possibly due to compaction. Bioclastic-oncolitic wackestone with mudstone/lime mudstone lenses (Facies 3) forms thin $(10 - 10$ cm) to medium $(10 - 30$ cm) beds with undulated bedding planes. In comparison with Facies 2, this facies is proportionally more

enriched in mudstone/lime mudstone and contains laterally variable but continuous mudstone/lime mudstone beds (< 5 cm). Oncoids and bioclasts are unevenly distributed in this facies.

The thick-massive grainstones/packstones (Facies 1) are interpreted to have formed in high-energy environments above fair-weather wave base, as evidenced by the presence of erosional bases in some grainstone beds and occurrence of cross bedding. The thick beds and persistent occurrence of this facies suggest deposition from a highenergy oncolitic-oolitic sand shoal complex close to the shelf margin (Fig. 6A). This is consistent with previous interpretations based on the regional distribution of oncolites (Gunn, 1998). Oncolitic-bioclastic packstone with mudstone/lime mudstone lenses/drapes (Facies 2) and bioclastic-oncolitic wackestone with mudstone/lime mudstone lenses (Facies 3) are interpreted as deposition from partially protected, distal tidal flat environments. The presence of thin (5 cm) lime mudstone/mudstone lenses may indicate progradational migration of back-barrier lagoonal deposits towards the shelf margin shoal complex (Fig. 6A).

3.2 Shallow lagoon facies association

The shallow lagoon facies association consists of oncolitic-bioclastic packstone with mudstone/lime mudstone lenses/drapes (Facies 2), bioclastic wackestone with mudstone/lime mudstone lenses (Facies 3), interbedded mudstone/lime mudstone with packstone interbeds (Facies 4) and bioclastic lime mudstone/mudstone (Facies 5). In comparison with the sand shoal facies association, this facies association is characterized by the decrease of grainstone and increase of lime mudstone and mudstone facies.

The packstone and wackestone facies (Facies 2 and 3; Table 1) form thin $(< 10$ cm) to medium (10-30 cm) beds with laterally discontinuous lime mudstone/mudstone lenses or thin $(< 5 \text{ cm})$ layers (Fig. 8C). Differential compaction leads to undulated bedding planes. Bioclasts are the main particle type, including well-preserved, centimeter-scale gastropods and *Receptaculites* (Fig. 9A and B). Oncoids are also present (Fig. 9B) but much less abundant than those in the sand shoal facies. The mudstone and lime mudstone facies (Facies 4 and 5; Table 1) occur as thin $($ 10 cm) beds, with variable wackestone/packstone layers/lenses (Fig. 8D). Differential compaction resulted in lateral thickness change, forming mottled texture (Fig. 9C and D). Well-preserved *Receptaculites* and gastropods are unevenly distributed and often penetrate through the lithological boundaries (Fig. 9C and D). Some crawling traces were found along the bedding planes of mudstone/lime mudstone, but they are often distorted or broken due to compaction.

The wackestone, lime mudstone and mudstone facies (Facies 3, 4, and 5) are interpreted as subtidal lagoon deposits likely formed below fair-weather wave base. Presence of packstone interbeds and detrital biolasts/oncoids in wackestone-limestonemudstone facies suggests sediment transportation by storm or high tidal waves. The thick packstone facies (Facies 2) was more likely formed in shallow-subtidal environments of the shallow lagoon, close to or above fair-weather wave base. The lagoon may have been restricted from open ocean by the oncolitic-oolitic sand shoal complex at the shelf margin (Fig. 6A), but it may have remained shallow, as evidenced by the close association with packstone and grainstone facies.

3.3 Shallow subtidal facies association

The shallow subtidal facies association consists of oolitic-peloidal grainstone and intraclastic-bioclastic grainstone-packstone (Facies 6 and 7; Table 1). Oolitic-peloidal grainstones form 0.3–1.0 m thick beds that commonly have minor erosional bases at the bottom. Small-scale (<20 cm) cross beddings are occasionally observed. Intraclasticbioclastic grainstones (e.g., Fig. 10D) form medium (10–30 cm) to thick ($>$ 30 cm) beds and have thin $(\leq 5 \text{ cm})$, laterally discontinuous shaly (muddy) partings along bedding planes (e.g., Fig. 8E). Intraclasts vary in size from 5 mm to 5 cm and are unevenly distributed; most of them have angular shapes (Fig. 8E) and composition of mudstone/lime mudstone.

The grainstone facies defined here refers to the facies appearing in the upper part of the measured section (113–184 m; Fig. 7). They are interpreted as deposits from shallow subtidal environments above fair-weather wave base in the proximal side of the shelf lagoon or in open shelf after the lagoon has been filled up. The presence of unsorted and angular intraclasts suggests intraclast formation in tidal flats and transportation into subtidal environments by storm waves or high tides.

3.4 Tidal flat facies association

The tidal flat facies association consists of mixed dolomite-limestones including bioclastic-peloidal wackestone, dolomitic lime mudstone with dissolution cavities, and microcrystalline dolostone (Facies 8, 9, and 10 in Table 1). Thin (10 cm) intraclasticbioclastic packstone (Facies 6 in Table 1) layers are also present. Bioclastic-peloidal wackestone (Facies 8) form thin (<10 cm) to medium (10–30 cm) beds with \leq 5-cm-thick

mudstone interbeds/lenses (e.g., Fig. 10C). A significant amount (up to 10%) of quartz and feldspar are present in both wackestone and mudstone interbeds (Fig. 10C). Bioclasts are unevenly distributed within lime mudstone matrix. Occasionally microbial laminae and fenestral structures are observed. Dolomitic lime mudstone (Facies 9) appears in thin $(\leq 10 \text{ cm})$ beds and less commonly, medium $(10-30 \text{ cm})$ beds, separated by yellowishreddish mudstone (e.g., Fig. 8F). Bioclasts are present but laterally variable in abundance and sizes. Dissolution cavities (e.g., Fig. 10E), vugs and "popcorn" quartz are found in some intervals. Microcrystalline dolostone (e.g., Fig. 10F) form thick (>30 cm) amalgamated beds containing vugs and cavities filled with white calcite crystals. Thin (< 3 cm) mudstone lenses/layers are also found in some intervals of the dolostone facies.

The wackestone, dolostone and dolomitic lime mudstone facies are interpreted as deposition from intertidal to supratidal environments as evidenced by shallow-water features including microbial laminae, fenestral structures, dissolution cavities, vugs, and siliciclastic components (quartz and feldspar). Thin packstone layers may have deposited during high tides or storm events.

METER-SCALE CARBONATE CYCLES

Three types of meter-scale cycles are identified from the measured section of the Antelope Valley Formation (Figs. 6B and 7). The sand shoal cycles have oncoliticoolitic-bioclastic grainstone facies (Facies 1) at the lower part and packstones/wackestone with mudstone/lime mudstone lenses (Facies 2 and 3) at the top. The change from massive grainstone to packstone/wackestone facies records a shallowing-up trend from subtidal to intertidal or progradation of lagoonal facies on the top of sand shoal facies during sea-level fall. Shallow lagoonal cycles consist of wackestone- and mudstone/lime mudstone-dominated facies (Facies 3, 4 and 5) in the lower part and packstone/grainstone (Facies 2) at the top, recording shallowing-upward trend from deep-subtidal (below fairweather wave base) to shallow subtidal (above fair-weather wave base) environments during sea-level fall. Peritidal cycles defined here refer to those from the upper part (113– 184 m) of the measured section (Fig. 7). They consist of packstone/grainstone facies (Facies 6 and 7) at the base and wackestone/lime mudstone/dolostone facies (Facies 8, 9, and 10) in the upper part, recording shallowing-upward trends from shallow subtidal to intertidal/supratidal environments. Exposure features are found only at the top of some peritidal cycles, but not in shallow lagoon and sand shoal cycles.

The *Receptaculites* sp. is present in the upper part of the sand shoal facies but is most abundant in the lagoon facies (82–113 m), suggesting their preference of living in lowenergy environments. The disappearance of *Receptaculites* sp. in the upper part of the measured section (113–184 m) also suggests that shallow-water environments with periodic exposure were not their environmental niche.

ISOTOPE RESULTS

In general, δ^{13} C values from the upper Antelope Valley Limestone Formation (Ope and Opf) are all negative (Fig. 7). From 0 m to 110 m, δ^{13} C values fall between -0.5‰ and -2.5% , with the majority of data points in the range of -1.0% $\sim -2.0\%$. Large δ^{13} C variations of -5.5% to -1.8% (average = -3.0%) are found from 110 to 170 m, followed by a slightly positive shift to -1.7% within the 14-m-thick dolostones immediately below the Eureka Quartzite (Fig. 7). The only positive δ^{13} C value of 0.06‰ is found at 178 m (8 m below the Eureka Quartzite), but because this is a single data point, its geochemical meaning needs further tests by sampling adjacent strata at much higher resolution.

The majority of $\delta^{18}O$ values from the measured sections fall between –6‰ and –8‰ (Fig. 7). Higher δ^{18} O values from -4.4% to -0.6% are found in the dolostone interval (172–186 m) below the Eureka Quartzite, exhibiting a "positive" shift (Fig. 7). However, because the reported isotope results did not correct the potential calcite-dolomite isotope fractionation (e.g., Rosenbaum et al., 1986; Dickenson et al., 1980), such a "positive" shift may record the oxygen isotope changes during dolomitization.

There is no $\delta^{13}C - \delta^{18}O$ co-variation when all the samples are considered together, but the $\delta^{13}C-\delta^{18}O$ patterns seem to vary with sedimentary facies (Fig. 11). The peritidal facies from 114 m to 172 m have the most diverse δ^{13} C values (-1.8‰ to -5.5‰) and least variable $\delta^{18}O$ (–5.5‰ to -7.5‰), while shallow lagoon and sand shoal facies (0–113 m) have both narrow $\delta^{13}C$ (mostly -1‰ to -2‰) and $\delta^{18}O$ (-6‰ to -8‰). In contrast,

the peritidal dolostone facies immediately below the Eureka Quartzite show an obvious δ^{13} C $-\delta^{18}$ O co-variation (Fig. 11).

Except for the dolostones below the Eureka Quartzite, there are no obvious lithology-dependent isotope variations (Fig. 12). Packstones and grainstones do have a slightly wider range of $\delta^{13}C$ (-5.5‰ to -0.5‰) and $\delta^{18}O$ (-6.0‰ to -8.5‰) than those of the lime mudstone ($\delta^{13}C$: -5.2‰ to -2.7‰; $\delta^{18}O$: -6.0‰ to -7.6‰) and wackestone $(\delta^{13}C: -4.7\%$ to -1.7% ; $\delta^{18}O: -5.5\%$ to -8.0%), but the isotope differences between adjacent lithologies are almost indistinguishable. In addition, no significant or systematic δ^{13} C or δ^{18} O changes have been found among lithologies of meter-scale cycles (e.g., Fig. 13), although the current sample resolution is insufficient to draw a general conclusion about cycle-related isotope variations.

DISCUSSION

6.1 The negative δ ¹³C 'excursion' below the unconformity: Not an oceanographic signature

The δ^{13} C profile of the Antelope Valley Limestone Formation in Arrow Canyon Range displays a negative 'excursion' with minimum δ^{13} C values down to $\leq -5\%$ below the basal unconformity of the Eureka Quartzite (Fig. 7). Negative δ^{13} C shifts down to –5‰ have been also documented from other sections in the Great Basin (Fig. 14), including the Shingle Pass and Ibex Hills sections (Edwards and Saltzman, 2014) and the Pahranagat Range, Hot Creek, and Lone Mountain sections (Kosmidis, 2009). However, in other global successions, time-equivalent strata have much less prominent negative δ^{13} C values. For example, Middle-Late Ordovician (Darriwilian–Sandbian; ca. 467–453 Ma) strata in Baltoscandia have δ^{13} C values mostly positive or close to 0‰ (Fig. 4; Ainsaar et al., 2010). The Middle-Late Ordovician strata from the Borenshult Drillcore in Sweden do not have negative δ^{13} C values or a negative δ^{13} C shift during Darriwilian (Bergström et al., 2012; Calner et al., 2014). The Middle-Late Ordovician strata in Western Newfoundland and sections from Precordillera of Argentina do not have $\delta^{13}C$ values lower than –2‰ (Thompson and Kah, 2011; Albanesi et al., 2013). Even in the Great Basin, Darriwilian strata in some sections such as the Monitor-Antelope Range section do not have negative δ^{13} C values lower than -2.5% (Fig. 4; Kump et al., 1999; Saltzman et al., 2005).

The δ^{13} C heterogeneity of Darriwilian strata in the Great Basin and across the globe (Figs. 4 and 14) suggests that the negative δ^{13} C 'excursion' below the Eureka Quartzite does not record a paleoceanographic signature. Instead, it may record a localized signature of a restricted basin or a diagenetic feature (e.g., Panchuk et al., 2006; Edward and Saltzman, 2014). Because local δ^{13} C variations up to -5% isotopic departure from open-ocean signature have been observed in modern lagoonal environments (e.g., Patterson and Walter, 1994; Swart et al., 2009), it can be argued that the negative $\delta^{13}C$ 'excursion' from the Arrow Canyon Range section was formed in a restricted environment. Facies analysis of the measured section (Figs. 6 and 7) and previous stratigraphic correlation (e.g., Gunn, 1998) suggest that the 30-m-thick stratigraphic interval from 82 m to 113 m was most likely deposited from lagoonal environments behind a shelf-margin shoal complex, but δ^{13} C values of that interval do not show significant changes in $\delta^{13}C$ (Fig. 7). In addition, the depth of the negative $\delta^{13}C$ 'excursion' below the Eureka Quartzite is highly variable (Fig. 14), from immediately below the Eureka Quartzite in the Lone Mountain section, to 25 m below the Eureka Quartzite in the Hot Creek Range, and to 50–150 m below the Eureka Quartzite in Shingle Pass, Ibex Hills, and Arrow Canyon Range sections. It seems that the negative δ^{13} C 'excursion' is more related to the stratigraphic position relative to the basal Eureka unconformity, rather than a particular facies deposited from restricted environments. The δ^{13} C $-\delta^{18}$ O patterns differ among the Great Basin sections (Fig. 15), with varying amount of data points falling into the lithification trend and burial diagenetic region of Knauth and Kennedy (2009). All these features indicate that the negative δ^{13} C shift of the uppermost Antelope Valley Limestone Formation was formed through various diagenetic alterations below an unconformity.

6.2 A diagenetic interpretation for the negative δ ¹³C 'excursion'

The variable δ^{13} C profiles (Fig. 14) and δ^{13} C $-\delta^{18}$ O patterns (Fig. 15) below the Eureka Quartzite suggest meteoric diagenetic alteration of isotope values with the development of vadose, freshwater phreatic, and mixing zones during the sea-level fall and exposure, similar to those documented from the Latest Devonian (Myrow et al., 2013) and Pliocene–Pleistocene (Swart and Kennedy, 2012) strata. In all those cases, absolute δ^{13} C and δ^{18} O values and their alteration depth below an unconformity may vary spatially, but a negative $\delta^{13}C$ shift is observed in most sections. The $\delta^{13}C - \delta^{18}O$ patterns and the depth of alterations may record variations of the paleo-water table and intensity of fluid-rock interactions (e.g., Allan and Matthews, 1982).

The co-variation of $\delta^{13}C$ and $\delta^{18}O$ from the uppermost 20 m of the measured section (Fig. 11) is similar to the $\delta^{13}C - \delta^{18}O$ pattern of the mixing zone of Allan and Matthews (1982) (Fig. 5D) and the burial diagenetic pattern of Derry (2010), but the close proximity to the base of the Eureka Quartzite suggests that this interval most likely records the isotope alterations of the paleo-vadose zone. The large δ^{13} C variations but limited δ^{18} O change from 114-170 m (Fig. 11) is similar to the general meteoric diagenetic pattern of Allan and Matthews (1982) (Fig. 5B) or the pattern close to the water table (Fig. 5C). Since the negative δ^{13} C 'excursion' mainly occurs in this interval, it suggests that the magnitude of δ^{13} C variations may have been controlled by the paleowater table. Since the depth of the paleo-water table may be controlled by the paleobathymetry or paleo-topography of the carbonate platform and lithologies (e.g., clay-rich layers) that can potentially serve as an aquifuge, the most intensively altered

 δ^{13} C interval could be meters to tens of meters below the unconformity. In this case, using the negative δ^{13} C shift to infer the ancient karstic uniformity requires additional physical stratigraphic evidence (cf., Cooper et al., 2001; Swart and Kennedy, 2012; Myrow et al., 2013).

The overall negative δ^{13} C and δ^{18} O values of the Antelope Valley Limestone Formation in Arrow canyon Range suggest overlapped diagenetic alterations. This is consistent with the presence of calcite twins in thin sections and oxygen isotope values mostly below –6‰ in the majority of the Great Basin sections (Fig. 15). However, the oxygen isotopes temporally vary in the same section and among sections at magnitudes of 4–10‰ (Fig. 15), using the $\delta^{13}C-\delta^{18}O$ crossplots of measured sections to screen out diagenetic samples, as many have used in the literature, is impractical and sometimes, misleading. The similar range of $\delta^{13}C$ and $\delta^{18}O$ variations in lime mudstones and grainstones (Fig. 12) also implies that the traditional practice of using fine-grained carbonates for isotope analyses unnecessarily improves the δ^{13} C record of stratigraphic successions. Instead, micro-recrystallization of lime mud (e.g., Fig. 10E and F) during diagenesis may lead to isotope alterations even more severe than in grainstones and packstones.

6.3 Implication for late Neoproterozoic negative δ ¹³C excursions

The presence of negative δ^{13} C shift with a nadir of -5.5‰ below the basal Eureka Quartzite adds to the notion that some of the prominent late Neoproterozoic $\delta^{13}C$ excursions may be related to meteoric diagenesis associated with sea-level fall and exposure (e.g., Knauth and Kennedy, 2009; Derry, 2010; Swart and Kennedy, 2012; Myrow et al., 2013; Oehlert and Swart, 2014). Although it is expected that meteoric

diagenesis is localized or regional and δ^{13} C anomalies of diagenetic origin should be less consistent and spatially variable as seen in the examples of Middle Ordovician (Fig. 14), Latest Devonian (Myrow et al., 2013) and Pliocene–Pleistocene (Swart and Kennedy, 2012), some of the Ediacaran δ^{13} C excursions do show large spatial variations. Examples include the Shuram-equivalent δ^{13} C excursion in South China (Doushantuo Member III, Jiang et al., 2007, 2008, 2011; Zhu et al., 2007, 2013; Lu et al, 2013) and in northern India (Krol B; Jiang et al., 2002; Kaufman et al., 2006) where (1) the thickness of strata that host the negative $\delta^{13}C$ excursion varies from a few meters to tens of meters; (2) $\delta^{13}C$ values vary from -5% to -12% ; and (3) $\delta^{13}C-\delta^{18}O$ patterns change from a positive covariance in some sections to large δ^{13} C but small δ^{18} O variations in other sections. These features are very similar to the $\delta^{13}C - \delta^{18}O$ patterns presented in this study and in other examples (e.g., Swart and Kennedy, 2012; Myrow et al., 2013). The variable diagenetic δ^{13} C $-\delta^{18}$ O patterns below unconformities (e.g., Fig. 11) cast doubt on the common practice of using the co-variation of δ^{13} C and δ^{18} O to screen out diagenetic samples (e.g., Kaufman and Knoll, 1995).

The Ediacaran Shuram $\delta^{13}C$ excursion in Oman was documented from a transgressive succession (e.g., Fike et al., 2006; Grotzinger et al., 2011). However, the negative δ^{13} C excursion from the upper Doushantuo Formation in South China has been variously ascribed as a transgressive sequence (e.g., Zhu et al., 2013) or regressive sequence (e.g., Jiang et al., 2007; Wang et al., 2014). The Shuram-equivalent $\delta^{13}C$ excursion in northern India (Jiang et al., 2002; Kaufman et al., 2006) mainly occurs in the regressive part of a sequence (Krol B). Apparently the relationships between late

Neoproterozoic $\delta^{13}C$ excursions and stratigraphic unconformities remain critical to interpret the origin of some unusually negative δ^{13} C excursions.

CONCLUSION

Sedimentological and isotope analyses of the Middle Ordovician carbonate-rich strata in the Arrow Canyon Range of southern Nevada, USA, reveal a negative $\delta^{13}C$ 'excursion' with a nadir down to –5‰ below a karstic unconformity at the base of the Middle-Late Ordovician Eureka Quartzite. Negative δ^{13} C values do not co-vary with δ^{18} O in general and seem to be lithologically independent. Similar negative δ^{13} C values have been documented from other correlative sections in the Great Basin but occur at variable depths below the basal Eureka Quartzite. The spatially variable δ^{13} C profiles and δ^{13} C- δ^{18} O patterns suggest meteoric diagenetic origin for the isotope anomaly that may have been controlled by the depth of the paleo-water table. While diagenetic $\delta^{13}C$ anomalies could potentially be used for stratigraphic correlation because they are associated with sea-level fall and exposure, the most intensive δ^{13} C alteration may happen at the stratigraphic interval close to the water table. The water table could be up to tenshundreds of meters below the unconformity, depending on the paleobathymetry/topography of the carbonate platform and lithologies that can serve as an aquifuge. Therefore, using negative δ^{13} C anomalies to track ancient sea-level fall/exposure requires integrated sequence stratigraphic and isotope analyses.

The presence of negative δ^{13} C anomalies below karstic unconformities in Ordovician strata and in many other stratigraphic intervals such as the Latest Devonian and Pliocene– Pleistocene strata add to the notion that some of the late Neoproterozoic negative $\delta^{13}C$ excursions may be of diagenetic origin. Typical examples may include the upper Doushantuo $\delta^{13}C$ excursion in South China and the Krol B $\delta^{13}C$ excursion in northern

India. In both cases 1Pc profiles show large spatial variations and variable $IPC-O^{18}O$ patterns similar to those presented in this study.

Facies	Constituents	Bedding	Sedimentary Structures	Interpretation
Thick-massive oncolitic- oolitic-bioclastic grainstone/packstone (1)	Spherical-oval oncoids of 3-10 mm in size. Oncoids constitute 5-50% of the grains. Ooids are 0.2-2 mm in size and vary in contents from 10-20%; occasionally up to 80%, forming oolite layers. Bioclasts are unevenly distributed, including brachiopod, gastropod, triolobite, and echinoderm fossil fragments. Occasional intraclasts consists of mudstone/lime mudstone.	Thick (30-100 cm) to massive $(> 1 \text{ m})$ beds. Erosional surfaces at the base and in cases, internal erosional surfaces are observed.	Cross-bedding is occasionally observed.	High-energy shallow subtidal oncolitic-oolitic sand shoals
Oncolitic-bioclastic packstone with mudstone/lime mudstone lenses/drapes (2)	Oncoids (3-10 mm) and bioclasts are the dominated grains. Oncoids constitute 5-30%; the rest of the grains are mixed bioclasts and peloids. Occasionally ooids can be seen.	Thin $(< 10 \text{ cm})$ to medium $(10-30 \text{ cm})$ packstone beds with laterally discontinuous, thin $(< 3$ cm) lime mudstone-mudstone beds/lenses or drapes.	Mudstone drapes; firmground (hardened lime mudstone).	Moderate- to high-energy peritidal environments close to shoal complex or subtidal lagoon
Bioclastic-oncolitic wackestone with mudstone/lime mudstone lenses (3)	Spherical and in cases, asymmetric oncoids and bioclasts unevenly distributed in lime mud matrix.	Thin $(< 10 \text{ cm})$ to medium $(10-30 \text{ cm})$ wackestone beds with laterally discontinuous lime mudstone-mudstone. Undulated bedding planes.	Mudstone drapes, bioturbation.	Moderate- to low-energy peritidal close to shoal complex or subtidal lagoon
Interbedded mudstone/lime mudstone with packstone interbeds (4)	Bioclasts (brachiopod, gastropod, trilobites, and echinoderm fragments) unevenly distributed in mudstone matrix. Some well- preserved gastropods and Receptaculites.	Thin $(< 10$ cm) beds. Packstone beds are laterally variable and have undulated bedding planes due to compaction.	Bioturbation; minor erosional surfaces at the base of packstones.	Protected, low-energy subtidal lagoon with storm events (packstones).
Bioclastic lime mudstone/mudstone (5)	Bioclasts unevenly distributed in mudstone and lime mudstone matrix. Some well- preserved Receptaculites.	Thin $(< 10 \text{ cm})$ undulated beds; some beds laterally pinches out within decimeter-meter distance	Bioturbation; occasional trace fossils.	Protected, low-energy subtidal lagoon environments
Oolitic-peloidal grainstone (6)	Ooids and peloids with minor bioclasts	Thick (30-100 cm) beds with erosional bases.	Occasional cross bedding.	High-energy shallow subtidal environments.

Table 1. Summary of facies of the upper Antelope Valley Limestone Formation in Arrow Canyon Range.

Table 2. Carbon and oxygen isotope results from the upper Antelope Valley Limestone Formation in the Arrow Canyon Range, southern Nevada, USA.

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FIGURE CAPTIONS

Figure 1. Location of study section. **(A)** Middle-Late Ordovician global reconstruction showing the paleolatitude of Laurentia (modified from Scotese and McKerrow, 1990) and location of the Great Basin (green star). (B) Location of the study section (green star) and other sections studied by previous researchers. 1. Nopah Range, CA; 2. Sheep Range, NV; 3. Pahranagat Range, NV; 4. Hot Creek Range, NV; 5. Monitor Range, NV; 6. Shingle Pass, NV; 7. Ibex Hills, UT.

Figure 2. Location of the study section in the Arrow Canyon Range.

Figure 3. Generalized Ordovician stratigraphic units in the Arrow Canyon Range. A major unconformity is assumed between the Eureka Quartzite and the Antelope Valley Limestone (Cooper and Keller, 2001). The Copenhagen Formation is missing in the Arrow Canyon Range, along with the top of the Antelope Valley Limestone. The measured section covers the uppermost Antelope Valley Formation, in which *Receptaculites* sp. are abundant (Ope and Opf; Langenheim et al., 1962).

Figure 4. Middle-Late Ordovician (Darriwilian–Sandbian; ca. 467–453 Ma) carbonate carbon isotope profiles in Baltoscandia (Ainsaar et al., 2010), Monitor-Antelope Ranges (Saltzman et al., 2005a; Kump et al. 1999) and Shingle Pass/Ibex Hills (Edwards and Saltzman, 2014). The red line represents the unconformity. MDICE and Chatfieldian are positive excursions.

Figure 5. Variation of $\delta^{13}C - \delta^{18}O$ patterns in meteoric diagenetic environments (after Allan and Matthews, 1982). (A) $\delta^{13}C - \delta^{18}O$ pattern at exposure surface. (B) Large $\delta^{13}C$ but small $\delta^{18}O$ variations of meteoric diagenesis in general; (C) Negative $\delta^{13}C$ shift but

no significant δ^{18} O variation close to the water table. (D) Positive co-variance of δ^{13} C and δ^{18} O in mixing zone.

Figure 6. (A) Depositional model for the facies associations of the upper Antelope Valley Formation (or uppermost Ope and Opf of Langenheim et al. (1962)). The lower part of the measured section (0–95 m; Fig. 7) is dominated by oncolitic-oolitic shoal complex and tidal flat facies. The middle part (95–113 m; Fig. 7) consists mainly of mottled muddy limestone/wackestone and bioclastic packstone/grainstone deposited from shallow-lagoon environments. *Receptaculites* sp. is most abundant in this interval. The upper part of the measured section (113–184 m) show a decrease of grainstone/packstone and increase of lime mudstone and dolostone, which were likely deposited from proximal peritidal environments. The measured section (Fig. 7) records a progradational sequence. **(B)** Three types of meter-scale cycles recorded in the measured section. The sand shoal cycles consist of grainstone/packstone in the lower part and packstone with muddy drapes/lenses/thin laminae in the top. The shallow lagoon cycles are composed of packstone with muddy lenses/laminae in the lower part and wackestone/lime mudstone/mudstone in the upper part, in which bioclastic packstone lenses or thin beds may be found. The tidal flat cycles have packstone/grainstone at the base but are dominated by low-energy, fine-grained limestone and dolostone (lime mudstone, mudstone, wackestone), with thin lenses of packstone/grainstone. Mudcracks and dissolution cavities are found in some of the tidal flat cycles.

Figure 7. Measured stratigraphic column and carbon-oxygen isotope profile of the upper Antelope Valley Formation (uppermost Ope and Opf) in the Arrow Canyon Range. The lower portion of the stratigraphic column (0–113 m) has relatively "stable" $\delta^{13}C$ values

(mostly between -2‰ and -1‰). In contrast, the upper part of the section (114–184 m) close to the unconformity at base of the Eureka Quartzite shows large δ^{13} C fluctuations from -1‰ to -5.5‰, possibly related to diagenetic alternations.

Figure 8. Representative facies of the upper Antelope Valley Formation (Opf). (**A**) Thick-massive oncolitic grainstone facies (at 76 m). (**B**) Oncolitic-bioclastic packstone with thin (< 3 cm) mudstone/lime mudstone lenses (at 72 m). (**C**) Bioclastic wackestone with mudstone/lime mudstone lenses (at 104 m). (**D**) Interbedded mudstone/lime mudstone with packstone interbeds (at 86 m). (E) Intraclastic-bioclastic grainstonepackstone (at 115 m). (F) Dolomitic lime mudstone with dissolution cavities and mud drapes (at 171 m).

Figure 9. Well-preserved *Receptaculites* sp. and gastropods in lagoon facies association. (**A**) *Receptaculites* sp. preserved in bioclastic-oncolitic packstone with mudstone/lime mudstone lenses (Facies 3) at 106 m. (**B**) *Receptaculites* sp. and gastropods preserved in bioclastic-oncolitic wackestone with mudstone/lime mudstone lenses (Facies 4) at 104 m; (**C**) *Receptaculites* sp. and gastropods preserved in interbedded mudstone/lime mudstone with packstone interbeds (Facies 4) at 107 m; (**D**) *Receptaculites* sp. and gastropods preserved in bioclastic lime mudstone/mudstone (Facies 5) at 108 m.

Figure 10. Thin section photomicrographs of carbonate facies from the upper Antelope Valley Formation (Opf). (**A**) Oncolitic-oolitic grainstone of the sand shoal facies at 71 m. Only part of an oncoid (Onc) is shown in the right. Notice the present of calcite twins (CT) indicates burial diagenesis and deformation, but the thin twins suggest deformation temperature < 170°C (e.g., Burkhard, 1993; Paulsen et al., 2007). (**B**) Bioclastic-peloidal

grainstone of the sand shoal facies at 72 m. Thin calcite twins (CT) are observed. (**C**) Bioclastic wackestone with thin mudstone layers/lens of intertidal facies at 120 m. Significant amount $(\leq 10\%)$ of silt-sized quartz and feldspar are present in both wackestone and mudstone layers. (**D**) Intraclastic-bioclastic grainstone of shallow subtidal facies at 128 m. Bioclasts include fragments of brachiopods, trilobites, bryozoans and calcium microbes. (**E**) Dolomitic lime mudstone with cavities (CF) of intertidalsupratidal facies at 135 m. The cavity is filled with coarser-grained dolomite, silt, and mud. (**F**) Microcrystalline dolostone of supratidal facies at 183 m. Notice that both the fine-grained matrix and bioclasts are partially dolomitized. All photos were taken under plane-polarized light. Scale bar $= 500 \mu m$.

Figure 11. The $\delta^{13}C - \delta^{18}O$ crossplot vs. facies associations. Notice that the majority of samples have $\delta^{18}O$ values falling between -6% ~ -8% but a wide range of $\delta^{13}C$ from -5.5‰ to -0.4 ‰. The peritidal facies from 114m to 172 m have the most diverse $\delta^{13}C$ values (-1‰ to -5.5‰) but least variable $\delta^{18}O$ (-5.5‰ to -7.5‰). In contrast, the dolostone facies immediately below the Eureka Quartzite show a co-variation of $\delta^{13}C$ and $δ¹⁸O.$

Figure 12. The $\delta^{13}C - \delta^{18}O$ crossplot vs. lithologies. Except for the dolostones immediately below the Eureka Quartzite that show co-varying δ^{13} C and δ^{18} O, there is no obvious lithology-dependent δ^{13} C and δ^{18} O trend.

Figure 13. The $\delta^{13}C$ and $\delta^{18}O$ variations in shallow lagoon and peritidal cycles. There is no significant or systematic change from the base to the top of cycles in these examples.

However, it should be pointed out that the current sample resolution is too low to test the meter-scale cycle-related isotope variations. Legends are the same as in Figure 6.

Figure 14. Carbon isotope variations below the Eureka Quartzite in the Great Basin (see Fig. 1 for location of sections). Negative δ^{13} C values down to $\leq -5\%$ are found in all measured sections but the depth of their occurrence below the basal Eureka Quartzite unconformity varies. In the Arrow Canyon Range section (this study), a negative $\delta^{13}C$ "excursion" (indicated by the dashed line) occurs 20–83 m below the unconformity. In Shingle Pass section (Edwards and Saltzman, 2014), δ^{13} C values show a minimum 80-100 m below the unconformity but low δ^{13} C values continue downwards. In Ibex Hills section (Edwards and Saltzman, 2014), a negative shift occur 0–50 below the Eureka Quartzite. In Pahranaghat Range section (Kosmidis, 2009), low (\leq -2‰) δ ¹³C values are present 10–50 m below the Eureka Quartzite but in Hot Creek Range and Lone Mountain sections (Kosmidis, 2009), low (\leq -2‰) δ ¹³C values appear only in strata 20–30 m below the Eureka Quartzite.

Figure 15. The $\delta^{13}C-\delta^{18}O$ crossplots of a few Middle Ordovician sections in the Great Basin (Nevada and Utah), with reference to the lithification and meteoric diagenetic trend (sky-blue band) of Knauth and Kennedy (2009). Each section below the Eureka Quartzite has points that plot along the meteoric diagenetic trend. (**A**) Arrow Canyon Range, Nevada (this study); (**B**) Monitor-Antelope Range, Nevada (Saltzman, 2005); (**C**) Shingle Pass, Nevada and Ibex Hills, Utah (Edwards and Saltzman, 2014); (**D**) Pahranaghat Range, Hot Creek Canyon, and Lone Mountain, Nevada (Kosmidis, 2009).

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