Local $\delta^{34}$S variability in ~580 Ma carbonates of northwestern Mexico and the Neoproterozoic marine sulfate reservoir

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Many $\delta^{34}$S records have been produced from carbonate-associated sulfate (CAS) in order to understand the oxidation state of the Neoproterozoic oceans, but interregional correlation is complicated by the absence of robust chronostratigraphic markers. Here, a globally correlatable stratigraphic interval containing the Wonoka–Shuram (W–S) $\delta^{13}$C excursion was analyzed to explore variability in the sulfur isotope record. In the excursion-containing units, the local $\delta^{34}$S record from multiple, closely spaced sections in Sonora, Mexico, was examined to explore potential heterogeneities, and then these were compared to more distant sections elsewhere.

In Sonora, the inception and isotopic minimum of the W–S excursion is located in the Clemente Formation and coincides with an extensive oolite marker bed. Five sections containing this marker bed span ~25 km of lateral distance, exhibit significant variability in $\delta^{34}$SCAS (range: +18.6 to +27.6, VCDT) and high variability in CAS concentration (range: <30 to >1200 ppm). Unlike the $\delta^{34}$SCAS values, CAS concentrations show strong negative correlation with Mn/Sr ratios and $F_{\text{Fe,carb}}$ concentrations, consistent with CAS removal upon diagenetic recrystallization and an absence of an accompanying sulfur isotopic fractionation. Indeed, samples containing low CAS concentrations exhibit petrographic characteristics consistent with diagenetic recrystallization including fabric destructive neomorphism and relatively coarse-crystalline textures.

Coeval W–S strata in Death Valley, Oman and the least altered Sonora samples record a decrease in $\delta^{34}$SCAS and an increase in CAS concentration; however, the magnitude of the changes are distinct, perhaps reflecting differential response to a transient oxidation event. In contrast, time equivalent facies of South China do not exhibit a decrease in $\delta^{34}$SCAS nor a relative increase in CAS concentrations. The variability in geochemical characteristics likely developed from local and/or regional marine $\delta^{34}$S_{sulfate} heterogeneity. Although Neoproterozoic oceanic heterogeneity in $\delta^{34}$S_{sulfate} has been proposed, it has not been reported on such close spatial scales. In addition, the existence of variability among the Sonora sections in which strata were all deposited at similar depth indicates that heterogeneity could have occurred laterally. Finally, these findings demonstrate that while CAS concentrations may be drastically affected by diagenesis, $\delta^{34}$SCAS may retain primary signatures.

1. Introduction

Stable isotopic compositions ($\delta^{13}$C and $\delta^{34}$S) of Neoproterozoic and Cambrian marine precipitates (i.e., limestones, dolostones and evaporites) display extreme stratigraphic trends (Fike et al., 2006; Gill et al., 2011; Halverson et al., 2005 and references therein; Hurtgen et al., 2004, 2005, 2009; Kaufman et al., 2007; Li et al., 2010; Loyd et al., 2012; McFadden et al., 2008; Xiao et al., 2012). The similarity in $\delta^{13}$C_{carb} values (the carbon isotope compositions of carbonates) among temporally equivalent rock units has prompted the use of carbon isotope chemostratigraphy as a correlation tool in the absence of biostratigraphic and radiometric constraints (Halverson et al., 2005). Unlike what is generally accepted for $\delta^{13}$C_{carb}, the $\delta^{34}$S_{sulfate} of evaporites and trace sulfate...
(carbonate-associated sulfate: CAS) in carbonate rocks have not been shown to be globally homogeneous, and yet many Neoproterozoic studies suggest that single basin trends in both δ^{13}C_{carb} and δ^{34}S_{sulfate} are related to global phenomena (cf., Fike et al., 2006; Fike and Grotzinger, 2008; Halverson et al., 2012; Halverson and Hurgen, 2007; Hurgen et al., 2005; Kaufman et al., 2007; McFadden et al., 2008). In more recent years, the hypothesis of a Neoproterozoic ocean with heterogeneous δ^{34}S_{sulfate} has gained support (see Lyons et al., 2012). Two styles of heterogeneity have been proposed, including vertical ocean stratification (or 'depth heterogeneity', Li et al., 2010; Shen et al., 2008, 2010, 2011; Xiao et al., 2012) and lateral variability ('horizontal heterogeneity', Hurtgen et al., 2006; Loyd et al., 2012; Lyons and Gill, 2008; Lyons et al., 2009, 2012). Indeed, lateral variability seems apparent when all of the available Neoproterozoic data are considered together, with the implicit assumption that the successions have not been altered through diagenesis. In order to better understand the Neoproterozoic ocean system, it is necessary to evaluate the extent of lateral sulfur isotope heterogeneity and determine if closely spaced, depth-equivalent stratigraphic sections record similar δ^{34}S_{CAS} signatures.

The most distinctive carbon isotopic event in Neoproterozoic time (and perhaps all time), is the so-called Wonoka–Shuram excursion (W–S), wherein carbonate δ^{13}C values plummet to −11‰ at ~580 million years ago (Ma; the purported age of an immediately underlying unconformity in Oman; Bowring et al., 2002) and exhibit a subsequent period of protracted carbon isotope recovery to values near 0‰ (e.g., Le Guerroue et al., 2006a). Whether a primary or secondary feature, the W–S provides a unique tie point, as it has been identified in many successions around the world, including Oman, Namibia, Australia, India, Brazil, Argentina, South China, eastern China, the southwestern United States and northwestern Mexico (Amthor et al., 2003; Bowring et al., 2007; Burns and Matter, 1993; Burns et al., 1994; Calver, 2000; Canfield et al., 2007; Condon et al., 2005; Corsetti and Kaufman, 2003; Fike et al., 2006; Gomez Peral et al., 2007; Grotzinger et al., 2011; Halverson et al., 2005; Jiang et al., 2007; Kaufman et al., 2006, 2007; Le Guerroue et al., 2006a,b; Loyd et al., 2012; Macdonald et al., 2009; McFadden et al., 2008; Nascimento et al., 2007; Nogueira et al., 2007; Prave et al., 2009; Sperling et al., 2007; Zhou and Xiao, 2007). Some authors have attributed the W–S event to either meteoric (Knauth and Kennedy, 2009; Swart and Kennedy, 2012) or burial diagenesis (Derry, 2010). However, the ubiquity of the excursion among multiple basins confirms its retained utility as a stratigraphic marker, regardless of its origin (see recent synopsis by Grotzinger et al. (2011)). Here, the W–S excursion is used as a synchronous stratigraphic tie-point to allow comparison of the δ^{34}S_{CAS} record locally, regionally and globally in order to better understand the nature of the sulfur cycle in Neoproterozoic time.

Carbonates of the Clemente Formation, Sonora, Mexico, record a very large magnitude negative carbon isotope excursion (expressing values down to −10‰ VPDB) and have been correlated to the W–S event (Loyd et al., 2012). The excursion-containing strata are exposed as a discrete, easily traceable marker bed and extend ~25 km laterally across three mountain ranges: Cerro Rajoń (CR), Cerro Clemente (CC) and Cerro Calaveras (CCv) (Fig. 1). Geochemical analyses among the three localities provide insight into the extent and variability of sulfur signatures during this time interval. Here, the lateral variability of CAS concentrations ([CAS]) and δ^{34}S_{CAS} in the marker bed are explored as well as their relationships to traditional proxies for carbonate diagenesis. The primary objectives of this study are to (1) examine the impact of diagenesis on CAS proxies (concentration and δ^{34}S_{CAS}) at the local scale, (2) explore the lateral variability of [CAS] and δ^{34}S_{CAS} at ~580 Ma and (3) provide an environmental interpretation of the least altered data.

2. Geologic setting

Neoproterozoic and early Paleozoic units crop out in northwestern Sonora, Mexico, primarily to the south of the town of Caborca (Fig. 1). These strata consist of mixed siliciclastic-carbonate successions that span the late Neoproterozoic to the latest Cambrian Furongian series (Fig. 2). Dominant sedimentary lithologies include dolostone, shale and quartzite with minor chert, basalt and limestone. Miogeoclinal deposits of Cerro Rajoń, the type section for Neoproterozoic units in northwestern Mexico (Stewart et al., 1984), unconformably overlie the Aibo Granite. The Aibo Granite comprises the basement rock for many of the passive margin deposits of the Sonora region and has been dated at ~1.11 Ga (Anderson et al., 1979; Rodríguez-Castañeda, 1994). Further chronological constraint is provided stratigraphically higher in the La Ciénega Formation where Cloudina has been reported (McMenamin, 1984, 1996; Sour-Tovar et al., 2007), representing an age of ~548 Ma (Corsetti and Hagadorn, 2000; Grotzinger et al., 1995). Within and above these Cloudina-bearing units, δ^{13}C_{carb} values express a short-lived negative excursion (Loyd et al., 2012), characteristic of Precambrian–Cambrian boundary sections worldwide (Corsetti and Hagadorn, 2000; Halverson et al., 2005). In agreement with a transition into Cambrian-aged rocks, Treptichnus pedum occurs in the lowermost member of the overlying Puerto Blanco Formation (see Fig. 2 for stratigraphic context; Sour-Tovar et al., 2007).

Approximately 200 m of massive to thinly bedded dolomite and sandy dolomite of the El Arpa and Caborca formations overlie the Aibo Granite. The contact between the El Arpa Formation and Aibo Granite is erosional and in some areas exhibits meter-scale incision. In addition, the lowermost El Arpa contains clasts of the Aibo Granite (also recognized by Anderson et al., 1979; Damon et al., 1962). The Clemente Formation occurs above the Caborca Formation at Cerro Rajoń and consists of ~200 m of siliciclastic facies with minor dolomite, sandy dolomite and limestone (Stewart et al., 1984). Approximately 133 m above the Clemente–Caborca contact lies a 2.6-m-thick carbonate marker bed composed of a basal oolite and upper, finely laminated micrite (Fig. 3; discussed in detail, below). A large-magnitude negative carbon isotope excursion occurs within the marker bed, with δ^{13}C values down to ~−10‰, and is likely correlative to the ~580 Ma W–S excursion based on its magnitude and stratigraphic position (Loyd et al., 2012). Above the marker bed, the Clemente Formation returns to primarily siliciclastic strata of alternating shales and quartzites with minor thin sandy dolomite beds. The Clemente Formation is conformably overlain by the ~75 mm thick fine- to medium-grained and commonly cross-bedded Pitiquito Quartzite (Stewart et al., 1984).

The aforementioned carbonate marker bed has been identified in nearly all mountain ranges of the Sonora region that host the Clemente Formation (Stewart et al., 1984). Sampled marker beds include two sections from Cerro Rajoń, two from Cerro Clemente (~15 km to the south–southwest of Cerro Rajoń) and one from Cerro Calaveras (~25 km to the southwest of Cerro Rajoń). Strata immediately under- and overlying the marker bed at each of these localities express nearly identical lithofacies compared to the Cerro Rajoń section. The strikingly similar expression of the δ^{13}C record in each of these marker beds is additional evidence for their contemporaneous deposition. Therefore, this marker bed presents an excellent opportunity for a case study to explore lateral variability over short distances in sulfur geochemical signatures during a well-defined Neoproterozoic time interval.

3. Materials and methods

Five stratigraphic sections of the carbonate marker bed were measured from three localities in the Caborca region: Cerro Rajoń (CR-1 and CR-2), Cerro Clemente (CC-1 and CC-2) and Cerro
Calaveras (CCv-1) (Fig. 1). Samples taken at regular intervals were analyzed for major and trace elemental concentration (Ca, Mg, Sr, Mn and Fe); carbonate-associated sulfate concentration; pyrite concentration and carbon, oxygen and sulfur isotope abundances ($\delta^{13}$C$_{\text{carb}}, \delta^{18}$O$_{\text{carb}}, \delta^{34}$S$_{\text{CAS}}$) (refer to Table 1 for geochemical data). Petrographic examination was conducted in order to confirm marker bed correlations using rare textures and structures and to document textural changes possibly associated with diagенesis.

3.1. Elemental analyses

Elemental analyses were conducted using an Agilent 7500ce ICP-MS after sample digestion in HNO$_3$ (2%). Ca and Mg contents are reported in weight percent (wt%), and Fe, Mn and Sr contents are reported in ppm compared to total carbonate content in each sample. Replicate analyses were better than $\pm 30$ ppm of reported values for Fe, Mn and Sr and better than $\pm 0.5$ wt% for Ca and Mg. The Ca/Mg values reported in Table 1 are molar ratios.

3.2. Carbonate-associated sulfate concentration

The CAS extraction method is modified after Burdett et al. (1989) and Marenco et al. (2008). Powdered rock samples were washed for 8–12 h four times in ultrapure (18 mΩ), de-ionized water and once in a sodium hypochlorite solution. Samples were not rinsed in NaCl solutions; however, these samples contain low pyrite concentrations and exhibit no evidence for secondary or primary sulfate minerals (anhydrite and/or gypsum) as confirmed by petrographic screening. Washed powders were acidified overnight in 3 M HCl in order to liberate lattice-bound sulfate (CAS) into solution as SO$_4^{2-}$. The samples were filtered down to 0.45 $\mu$m to remove insoluble residues, which were then quantified gravimetrically. The mass of the insoluble residue mass was subtracted from the initial powder mass in order to quantify weight percent carbonate (assuming that all of the dissolved material was pure carbonate). The supernatant fluids were heated to $\sim$70°C, and a 30% BaCl$_2$ solution was added to induce precipitation of barite. Precipitation occurred at room temperature for 72 h in order to ensure reaction completion. The precipitated barite was removed via filtration, with the resulting mass determined gravimetrically. Sulfate concentrations were calculated based on the mass of barite, and [CAS] is reported in parts per million (ppm) within the carbonate fraction in each sample by correcting for the amount of insoluble material. Duplicate measurements of [CAS] were within $\pm 15\%$ for individual samples.

3.3. Pyrite concentration

Pyrite concentrations were determined via the chromium reduction method described by Canfield et al. (1986). Two-gram
Fig. 2. Stratigraphic column of Neoproterozoic units from Cerro Rajón. Zoom-in provides stratigraphic context of marker bed facies. The marker bed exhibits carbon isotope values consistent with the −580 Ma Wonoka–Shuram (W–S) global negative excursion. Scale bar corresponds to the left hand column. Age constraints are discussed in detail in text.

splits of the insoluble residues acquired from CAS extraction were reacted in a 1 M CrCl₃/HCl solution under a N₂ atmosphere. The product H₂S (gas) was passed into a trap containing a 3% AgNO₃/10% NH₄OH solution and captured as solid-phase Ag₂S. The precipitated silver sulfide was filtered from solution and quantified gravimetrically. Pyrite concentration was then calculated stochiometrically and reported as weight percent (wt%) compared to the original total powder mass. Replicate analyses were consistent within ±10% of the values reported here. Many replicate analyses consistently produced very low pyrite concentrations, and therefore δ³⁴S_pyr could not be determined.

3.4. Isotopic analyses

3.4.1. Carbon and oxygen

Carbonate carbon and oxygen isotope analyses were conducted at the University of Southern California using a VG Prism II IRMS. Samples were microdrilled from thin section billets after petrographic characterization. Replicate measurements are better than 0.1‰ for both carbon and oxygen. Oxygen and carbon isotope values are recorded in the standard δ notation in comparison to the VPDB standard.

3.4.2. Sulfur

Sulfur isotope analyses were conducted on a ThermoScientific Delta V Plus IRMS in the Laboratory of Biogeochemistry at the University of California, Riverside. The IRMS is interfaced with a Costech Analytical Technologies Inc., elemental combustion system via a Thermoscientific CONFLO III interface. Sulfur isotope values are reported in the standard δ notation in comparison to the VCDT standard. Interlaboratory comparison with the University of Maryland reveals agreement better than ±0.5‰, and replicate analyses within the individual labs yielded values consistently within ±0.1‰.
4. Results

4.1. Marker bed petrography

The carbonate marker bed (Fig. 3A) of the Clemente Formation exhibits a laterally consistent lithostratigraphic progression in addition to similarities in sedimentary structures, textures and microfabrics. The lowermost marker bed interval consists of basal oolite overlying reddish-brown quartzite in gradational contact (Fig. 3B–D). A buff to pinkish-gray dolostone with highly elongate intraclasts of dolomite and/or pinkish-gray limestone occurs above the oolite in most places (referred to here as flat-pebble conglomerate or FPC; Fig. 3E). A fine-scale, wavy laminated dolostone/limestone (Fig. 3F) overlies the FPC. Finally, the laminated interval is overlain by purple shale in depositional contact. At sample sites CCv-1 and CC-2, the FPC is absent, and the laminated interval is in direct contact with the underlying oolite. At CC-1, the FPC occurs between two discrete laminated horizons. Each major lithologic interval is described in detail below.

4.1.1. Oolite interval

The lowermost buff-colored oolite ranges in thickness from ~60 to 270 cm. Horizons of matrix-supported conglomerate occur within the oolite. Conglomerate clasts are typically 1–10 cm in diameter, subrounded to rounded and are composed of dolomitic oolite or buff-colored dolomite (Fig. 3B). Elongate rip-up clasts (Fig. 3C) as well as multiple-generation compound ooids (creating grains up to ~3 mm in diameter; Fig. 3D) occur within the oolite interval.

Individual ooids range in diameter from ~100 to 700 μm and are circular to oval in cross section (Figs. 4A and 5A). In well-preserved samples, ooid cortices display a radial-concentric fabric typical of
ancient ooids (e.g., Sandberg, 1975), and anhedral spar or banded cements fill the interstices between ooids. Where present, bladed cements exist as isopachous rims and are followed by the sparry, later-generation cement (Fig. 5A and B). Some samples do not exhibit bladed cements and are cemented entirely by blocky spar (as in Fig. 3D). Pervasive neomorphism has preferentially affected samples of CC-2 and CCv-1 versus the other localities, such as the ooids/cements are less clearly defined but still discernable (Fig. 5C).

4.1.2. Flat-pebble conglomerate interval

The middle member of the marker bed sequence is composed of buff to reddish-gray, matrix-supported, limestone/dolostone conglomerate. The intraclasts are primarily composed of redgray limestone, are highly elongate and have length-to-width aspect ratios >10:1. In addition, intraclasts display a wide range of spatial orientations with inclinations between 0° and 90° compared to bedding (Fig. 3E). The matrix consists of buff-colored micrite and micropar in an interlocking mosaic. The thickness of the FPC interval is variable and ranges from being completely absent to a thickness of ~1 m. Lateral examination reveals that the FPC exhibits a lensoidal or otherwise discontinuous morphology. In rare cases, the upper laminated facies are interrupted by relatively thin intervals of FPC.

4.1.3. Laminated interval

The uppermost member of the marker bed consists of finely laminated, purple-gray to buff-gray micritic dolomite and limestone (Fig. 3F). Lamina thickness and purple coloration tend to decrease upward such that lamination is difficult to distinguish in outcrop in the uppermost centimeters. The lamination is defined by horizontal distributions of opaque inclusions or by differences in carbonate crystal size.

At study sites CR-1, CR-2 and CC-1, the laminated facies contain upwardly domed structures with fan-like morphology (Figs. 4B,C and 5D). These “fans” consist of ~100–150 µm tall, radiating crystals with blunt terminations (Fig. 4D). In rare cases, clusters of opaque grains accumulate near the basal portions of larger crystal projections. Bedding-parallel thin sectioning exposes crystal tops with pseudohexagonal morphologies (Fig. 4E). Fans tend to occur in high abundance along particular horizons (Fig. 6), but in some cases isolated fans exist as well. In samples from
4.2. Geochemistry

4.2.1. Carbon and oxygen isotopes

All five sample sites display similar trends in carbon and oxygen isotope values (Fig. 7). Oxygen isotope compositions begin at ∼−8‰ (VPDB) in the basal oolite and decrease to a minimum of ∼−13‰ in the uppermost laminated interval. Carbon isotopes show a similar trend, except minima typically occur near the basal or middle portions of the laminated interval. Minimum δ13C values in all sections fall below −8‰ (VPDB). δ13C values from CR-1 and CR-2 include the lowest measured, with minima as low as −9.5‰. δ13C and δ18O show moderate positive correlation (Fig. 8).

4.2.2. Elemental concentration

Stratigraphic analyses of the trace elemental concentrations of Sr, Mn and Fe (referred to as Sr_{carb}, Mn_{carb} and Fe_{carb}, respectively) and major elements Ca and Mg reveal general similarities among the five sample sites (Fig. 7). Strontium concentrations...
are low and range from 80 to 208 ppm in the basal oolite interval and increase to maximum concentrations between 134 and 323 ppm in the middle to uppermost portions of the laminated interval. The higher resolution sample sites (CR-1 and CR-2) show a pronounced increase in Sr\textsubscript{carb} coincident with the transition into the laminated member. Sample site CCv-1 does not exhibit an increase in Sr\textsubscript{carb}, and instead concentrations decrease slightly up section.

In all sections, Mn\textsubscript{carb} concentrations fall between 289 and 2636 ppm. CR-1 displays elevated Mn\textsubscript{carb} concentrations (between 1139 and 2636 ppm) within the FPC interval and a sharp decline (from 1918 to 982 ppm) coincident with the transition into the laminated interval. A less pronounced increase is evident at 120 cm in the FPC interval of CR-2, where Mn\textsubscript{carb} concentrations reach 2250 ppm.

In general, Fe\textsubscript{carb} concentrations decrease up section with the exception of CCv-1. Sample sites CR-1 and CR-2 show pronounced increases in the FPC interval. Basal Fe\textsubscript{carb} concentrations are typically high (except CR-1), with values >3000 ppm and up to 5582 ppm. Concentrations are unknown in the uppermost portion of the laminated interval.
lower in the laminated interval (with the exception of the uppermost CCv-1 data point), with values between 449 and 1594 ppm.

Aside from CCv-1, Mn/Sr ratios are relatively low in the upper laminated interval (between 0.7 and 5.4). Sample sites CR-1, CR-2 and CC-1 show a pronounced increase near the middle of the section, coincident with the FPC (CR-1 and CR-2) or lower laminated (CC-1) members. Mn/Sr values of CCv-1 increase from 4.5 in the basal oolite to 18.2 in the laminated member.

The lowermost samples of each section yield relatively high Mg/Ca (molar) ratios, approaching 1—the value of stoichiometric dolomite. These values generally decrease up section, and the laminated facies exhibit ratios near zero. One exception is site CCv-1, where the uppermost data point has a Mg/Ca ratio of 0.47.

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**Fig. 7.** Geochemical data shown stratigraphically for all five sections. Refer to Fig. 2 for stratigraphic key. Three fan icons indicate abundant crystal fans. A single fan icon indicates rare crystal fans. Fan icons with an overlying R indicate recrystallized fan horizons. Strontium concentrations are elevated 10\(^\times\) to enhance visualization of stratigraphic trends. Mg/Ca diagrams are separated as follows: light gray = Mg/Ca ratio consistent with low Mg calcite (LMC), gray = high Mg calcite (HMC), far right of dark gray = dolomite (DOL; Mg/Ca = 1). Notice similarity in stratigraphic trends of \(\delta^{13}C_{\text{carb}}\) and \(\delta^{18}O_{\text{carb}}\) and relative lack thereof in [CAS] and \(\delta^{34}S_{\text{CAS}}\). The negative trend in \(\delta^{13}C_{\text{carb}}\) up-section is likely the Wonoka–Shuram excursion, recognized in ~580 Ma carbonates elsewhere.
4.2.3. Carbonate-associated sulfate and pyrite

Carbonate-associated sulfate ([CAS]) are highly variable among the different stratigraphic sections (Figs. 7 and 9). Sites CC-2 and CCv-1 exhibit extremely low values, falling below 30 ppm. [CAS] values of CR-1 show a minimum near the basal FPC and elevated concentrations of ~400 ppm in the basal and uppermost horizons of the section. CR-2 displays high [CAS] (~500 ppm) in the upper portion of the laminated interval and uppermost oolite/lowermost FPC (~300 ppm) and low values (<49 ppm) elsewhere. CC-1 exhibits the highest [CAS], with values in excess of 1000 ppm in the laminated interval. Pyrite concentrations are low, with all samples containing less that 0.01 wt% (Supplementary Fig. 1).

Supplementary material related to this article found, in the online version, at http://dx.doi.org/10.1016/j.precamres.2012.10.007.

4.2.4. $\delta^{34}S_{\text{CAS}}$

The sulfur isotope composition of CAS varies moderately within and among the different sections studied (Figs. 7 and 9). In total, $\delta^{34}S_{\text{CAS}}$ values range from +18.6 to +27.6‰. Samples from the lower portion of the section range from +18.9 (CR-1) to +27.6‰ (CC-1), mid-section samples range from +21.5 (CR-2) to +23.3‰ (CR-1), and the upper samples range from +20.6 (CR-1) to +25.5‰ (CC-1). Sample site CC-2 lacked sufficient CAS to perform isotope analyses, and only one sample from CC-1 yielded sufficient CAS, thus stratigraphic trends could not be developed at these sites.

5. Discussion

5.1. Marker bed depositional environment

Inter-outcrop consistencies in the succession of lithologic characteristics, as well as similar suites of depth-restricted sedimentary structures, suggest that all of the marker bed sections were deposited at similar paleo-depths. The occurrences of multiple-generation and large compound ooids, rip-up clasts and conglomeratic components within the oolite interval suggest a relatively high-energy, wave- and/or tide-influenced shallow depositional environment. Specifically, the multiple-generation, compound ooids indicate that these grains were probably not
transported significant distances from the ooid forming environment, which implies a very high energy regime with recurring resuspension of already-cemented ooids. The FPC interval is additional evidence for deposition at a very shallow depth with little post-formation clast transport (FPC’s are generally interpreted as intra-formational structures).

The laminated component most likely represents a relatively deeper or more protected depositional environment. Although lamination is not depth-dependent per se, its presence together with the absence of cross-bedding, cross-lamination and channels does suggest a relatively low energy system, interpreted here as deeper than the underlying oolite and FPC.

Because this succession of sedimentologic characteristics is repeated at all of the studied sites, we can surmise that these marker beds were deposited under similar physical conditions, perhaps representing shallow oscillatory-flow-dominated paleoenvironments. Therefore, geochemical comparison among these sites may provide insight into lateral variability in ocean chemistry, provided that methodological artifacts and diageneric alteration can be ruled-out and/or isolated (see below).

5.2. Pyrite oxidation and the reliability of CAS in carbonates

Marenco et al. (2008) and Mazumdar et al. (2008) demonstrated that pyrite oxidation during the CAS extraction procedure can alter the primary values of both [CAS] and $\delta^{34}$S$_{CAS}$. Fortunately, the low pyrite concentrations in marker bed carbonates (all samples <0.01 wt%) make alteration of this sort unlikely. Furthermore, [CAS] and $\delta^{34}$S$_{CAS}$ do not correlate with pyrite concentration (Supplementary Fig. 1A and B). Petrographic screening did not reveal any sulfate minerals, which would be expected to form as a result of non-methodological pyrite oxidation (in outcrop, for example). Thus, while pyrite oxidation can obscure CAS data in carbonate rocks (either during sample analysis or post-depositional alteration), it does not appear to have significantly altered those of the Clemente marker bed.

![Fig. 8](image_url) Cross plot of $\delta^{13}$C$_{carb}$ and $\delta^{18}$O$_{carb}$ for all samples. Notice positive correlation.

![Fig. 9](image_url) Composite $\delta^{13}$C$_{carb}$, $\delta^{34}$S$_{CAS}$ and CAS concentration curves for the five Sonora study sites and those of the Rainstorm carbonates (DV). Here, sulfur curves are time-correlated via $\delta^{13}$C. Notice the moderate variability in $\delta^{34}$S$_{CAS}$ and high variability in CAS concentration. $\delta^{34}$S$_{CAS}$ and CAS concentration are significantly reduced and elevated, respectively, compared to underlying and overlying carbonates at Cerro Rajón. Gray envelopes encompass Sonora sulfur isotope and [CAS] data.
5.3. Diagenetic indicators

Although pyrite oxidation does not seem to be a major issue here, other styles of alteration during burial and their potential impacts on [CAS] and δ[^1][S][CAS] must be considered. Sr[carbonate], Mn[carbonate] and Fe[carbonate] are traditionally used to assess the degree of alteration in carbonate systems due to the their relative concentrations in marine, meteoric and burial diagenetic fluids and their affinity to the carbonate crystal lattice (Bodine et al., 1965; Brand and Veizer, 1980; Kinsman, 1969; Turekian, 1972). Progressive meteoric alteration of originally marine carbonates generally leads to a decrease in Sr[carbonate] and an increase in Mn[carbonate] (Brand and Veizer, 1980). In addition, meteoric as well as burial diagenesis can produce decreases in both carbon and oxygen isotope compositions (Allan and Mathews, 1982; Banner and Hanson, 1990; Derry, 2010; Knauth and Kennedy, 2009; Turekian, 1972). Along with decreased δ[^1][C][carbonate] and δ[^1][8][O][carbonate] values, significant Fe[carbonate] enrichments are generally attributed to recrystallization with increasing burial (e.g., Tucker and Wright, 1990).

Textural changes are also expected during progressive diagenetic alteration. In general, crystal size increases with increasing recrystallization such that the crystallographic progression should follow the trend from micrite to microspar to pseudospar in carbonates experiencing alteration (Brand and Veizer, 1980). This crystal growth has been termed aggrading neomorphism (Bathurst, 1975; Folk, 1965) and has been recognized in many carbonate systems. In addition, intricate textural features can be destroyed upon recrystallization. However, previous reports of Precambrian carbonates demonstrate that dolomitization can preserve some textures through a process known as mimetic dolomitization (Corsetti et al., 2006; Sibley, 1991; Tucker, 1983; Zempolich and Baker, 1993), wherein original sedimentary and/or crystallographic fabrics are preserved during the subsequent dolomitization.

Research by Gill et al. (2008) provided a first step toward understanding the effects of diagenesis on CAS proxies (concentrations and δ[^3][S][CAS]). In that study, the authors demonstrated that meteoric recrystallization of Pleistocene coralline aragonite to low-Mg calcite is accompanied by significant decreases in δ[^1][8][O][carbonate], Sr[carbonate], Na[carbonate] and [CAS]. In contrast, δ[^3][S][CAS] values are relatively invariant between primary and recrystallized phases, suggesting that the sulfur isotope compositions are buffered to primary values. These findings led the authors to conclude that meteoric recrystallization can cause a reduction in [CAS] but that δ[^3][S][CAS] is relatively unaffected and can preserve primary δ[^3][4][S][sulfate] values.

5.4. Marker bed diagenesis and CAS concentration

Upon petrographic examination, it is clear that the marker beds were influenced by at least two distinct phases of diagenesis. The earlier phase corresponded to extensive oolite cementation, likely in a mixed marine–meteoric environment. This interpretation is supported by the paragenetic evolution from framework grains (oooids); followed by bladed, isopachous cements and finally blocky spar that occluded the remaining pore space (Fig. 5A and B). Such a progression is common in marine carbonates experiencing cementation during increased meteoric influence (Bathurst, 1975). The later stage(s) of diagenesis was associated with primary fabric destruction and has seemingly influenced each marker bed section to different degrees. Fig. 5B–F displays the degree of fabric destruction associated with this later period of diagenesis and its relative influence on the marker bed carbonates. The effects of late recrystallization (often described as ‘increased textural maturity’) are discussed further below, along with notable geochemical variability.

Values of [CAS] correlate inversely with Fe[carbonate] and Mn/Sr (Fig. 10). These trends are consistent with meteoric and/or burial alteration of an initially marine-precipitated carbonate, as explained above. These results are in broad agreement with those of Gill et al. (2008) in that [CAS] decreases upon recrystallization.

Samples and sections exhibiting aggrading neomorphism and lacking well-defined intricate features (crystal fans, laminae and ooid cortices) exhibit low to negligible [CAS] and were likely influenced by burial diagenesis. Specifically, CC-2 and CCv-1 display [CAS] values below 30 ppm and lack well-pronounced crystal fans. CC-2 contains “fan-like” features (Figs. 4F and 5E); however, these are characterized by a coarse-crystalline, anhedral mosaic suggestive of significant aggrading neomorphism. Fan blades in CC-2 do not exhibit well-pronounced straight edges, in contrast to those of CR-1, CR-2 and CC-1, which is also indicative of recrystallization. CCv-1 contains no fans nor fan-like features and lacks a well-defined lamination (Fig. 5F). The lamination can be seen in outcrop, however, lamina transitions are obscure, and the boundaries are diffuse. In photomicrograph, the laminated facies are composed of pseudospar, likely reflecting aggrading neomorphism of a finer-grained precursor (probably micrite). In addition, the oolithic interval of CCv-1 is composed of a pseudospar mosaic, and ooids are identifiable but appear ghost-like (Fig. 5C), suggestive of recrystallization.

The above observations indicate removal of CAS during recrystallization again in agreement with the findings of Gill et al. (2008). Elevated Mn/Sr and Fe[carbonate] and increased textural maturity show strong correlation with decreased [CAS]. The overall low Sr[carbonate]
and higher concentrations of Mn_{carb} (290–2640 ppm) and Fe_{carb} (490–5700 ppm) are indicative of diagenetic influence in all intervals of the marker bed. Therefore, the samples with the lowest Mn/Sr ratios and Fe_{carb} and highest [CAS] are likely the best candidates for recording the primary geochemistry of coeval seawater.

It is notable that the oolite intervals of the marker beds in the most unaltered sections generally contain significantly less CAS than the corresponding laminated intervals (Fig. 7A–C). Given that the oolite interval contains a large proportion of bladed and/or blocky cements (~20% in some cases), it is likely that a large amount of carbonate was derived from a meteoric fluid (Bathurst, 1975). Since meteoric fluids contain relatively low concentrations of dissolved sulfate, it seems reasonable that the oolites would contain less CAS. As a result, the marine-dominated fan interval should be more representative of a primary marine precipitate and therefore is the primary target in our effort to reconstruct past seawater sulfate concentrations.

5.5. Diagenetic effects on $\delta^{34}$SCAS

The isotopic composition of CAS is moderately variable among the sample sites. $\delta^{34}$SCAS shows no appreciable correlation with Fe_{carb}, Mn/Sr or CAS concentration (Fig. 11A–C), further supporting that diagenesis has not significantly affected the sulfur isotope composition of CAS (as proposed in Gill et al., 2008). Ultimately, the variability in $\delta^{34}$SCAS at marker bed sites may result from primary local heterogeneity in seawater $\delta^{34}$S_{sulfate} or later, diagenetic modification during burial. Whereas diagenesis has not been conclusively identified as a $\delta^{34}$SCAS modifying process (cf., Gill et al., 2008; Lyons et al., 2004), at first glance it seems likely that diagenetic processes could preferentially affect $\delta^{34}$SCAS versus $\delta^{13}$C_{carb}, given the very high carbon content and therefore greater rock-buffering tendencies in carbonates (Banner and Hanson, 1990). However if considered further, burial diagenesis (as well as meteoric diagenesis, see Gill et al., 2008) can be ruled out as a probable modifier of the $\delta^{34}$SCAS signal, particularly if the concentration of sulfate in diagenetic fluids is considered. Although it is difficult to characterize burial diagenetic waters, it is likely that these fluids were low in sulfate (particularly if Precambrian seawater contained low sulfate and given that sulfate-rich formation waters are generally sourced from seawater) and therefore the potential for burial alteration of the $\delta^{34}$SCAS signal was probably quite limited. Thus, we prefer a primary origin of the $\delta^{34}$SCAS signal and posit that the variability observed within the oolite marker beds reflect oceanic heterogeneity in marine $\delta^{34}$S_{sulfate}.

5.6. Local seawater sulfate and $\delta^{34}$S

Although diagenetic overprinting can remove CAS, it is encouraging that samples from Neoproterozoic units retain at least some and occasionally high residual CAS. The implication is that Neoproterozoic seawater contained appreciable sulfate levels to be preserved in solid-phase carbonate. However, deriving precise sulfate concentrations in Neoproterozoic seawater (liquid concentration, mol/L) is impossible given only [CAS] in parts per million (solid concentration g/10^6 g), especially without well-known partition coefficients. Nevertheless, relative changes in concentrations of seawater sulfate using both [CAS] and $\delta^{34}$SCAS data should provide useful information. Specifically, we will compare inter-site geochemical trends for the marker bed using the $\delta^{13}$C_{carb} record and the general lithologic intervals as correlation tie-points. The similarities in lithology and depositional depth among individual marker bed sections and intervals provide a scenario whereby geochemical variability is not likely the result of facies variability or a vertically stratified water column and therefore these sites represent an excellent case study to explore local, lateral heterogeneity.

Values for [CAS] within the marker bed at CR-1, CR-2 and CC-1 are significantly elevated compared to units stratigraphically above and below (see Fig. 5 in Loyd et al., 2012). Non-marker bed Neoproterozoic carbonates of Cerro Rajón exhibit CAS concentrations <200 ppm (Loyd et al., 2012), in striking contrast to marker bed values of up to 1200 ppm. The increased [CAS] of the marker beds are not likely a strict consequence of a facies-dependence.
on sulfate incorporation and/or preservation in carbonate rocks. This is due to the fact that similar lithologies (i.e., oolites, finely laminated carbonates, etc.) within the sections but not associated with the marker beds record consistently low [CAS]. However, the incorporation of sulfate into the carbonate crystal lattice is still poorly understood and additional research must be conducted along these lines. Nevertheless, the increase in [CAS] observed here and elsewhere in contemporaneous units, along with coeval trends in isotope records, make an at least partial primary origin for these signals reasonable, as discussed below.

As with the marker beds in Sonora, an increase in CAS concentration of similar magnitude is observed in time-equivalent carbonates of the Rainstorm Member (Johnnie Formation) in the Death Valley region (Fig. 9; Kaufman et al., 2007). The Rainstorm carbonates also contain similar lithologic transitions (oolite lying stratigraphically below a finely laminated carbonate) and enigmatic fabrics (FPC and formerly aragonitic crystal fans; Corsetti and Kaufman, 2003; Pruss et al., 2008). The increased [CAS] in ~580 Ma carbonates from Death Valley and Sonora may reflect a transient increase in seawater sulfate. The spatial scale of this increase is difficult to constrain, and extrapolation to a global increase in marine sulfate is far from justifiable given the lack of [CAS] data from additional, more distant localities and the growing likelihood of a globally heterogeneous Neoproterozoic ocean (Hurgen et al., 2006; Loyd et al., 2012; Lyons and Gill, 2008; Lyons et al., 2009, 2012). However, the [CAS] increases in Sonora and Death Valley carbonates do indicate some degree of continuity over ~800 km of lateral distance—or less, if one accepts the Sonora-Mojave megashear hypothesis, which suggests that Sonora and Death Valley were subsequently displaced from one another along a major, now obscured, fault zone (cf., Anderson and Silver, 2005; Stewart, 2005).

Sulfur isotope values for CAS from the Clemente marker bed show somewhat differing stratigraphic trends among the five sections studied (Figs. 7 and 9). Section CC-1 has a δ^{34}SCAS trend similar to that of the Rainstorm Member carbonates of Death Valley, with isotope values decreasing ~7–10‰ near the middle to upper portions of the section (Kaufman et al., 2007). CR-2 also exhibits a mid-section decrease in δ^{34}SCAS; however, a less severe increase of ~3‰ occurs in the lower 60 cm of the marker bed. Finally, section CR-1 displays an overall increase in δ^{34}SCAS, with a mid-section maximum of ~23‰ (it is important to note that this is still lower than non-marker bed carbonates of the Clemente Formation of Cerro Rajón). The observed differences among the Clemente marker beds demonstrates very localized variability in δ^{34}SCAS (Hurgen et al., 2006) also report significant variation in δ^{34}SCAS among sections of the Namibian Maienberg cap carbonate (Mariñoan) separated by ~200 km of lateral distance. However, these authors also noted good agreement in δ^{34}SCAS among nearby sections of the same unit. The younger (~580 Ma) carbonates of the Clemente marker bed show significant variability (up to 9‰) over a mere ~25 km of lateral distance, suggestive of localized controls on seawater δ^{34}S sulfate.

Despite differences in the details, the five Sonora sections and the one Death Valley section record similar stratigraphic trends. While the Death Valley section exhibits a siliciclastic interval between the lower oolite and upper fan-bearing carbonates (Corsetti and Kaufman, 2003), the Sonora sections all contain a basal oolite directly overlain by hummocky cross-stratified, fan-bearing, pink carbonate. Therefore, the Sonora carbonate marker beds represent equivalents deposited at essentially the same depth. The variation in δ^{34}SCAS among the five sections indicates that lateral variability is δ^{34}S sulfate (as opposed to vertical variability potentially arising from a stratified water column) could have existed at ~580 Ma, even across short lateral distances.

5.7. The Clemente and Rainstorm W–S facies: a paleoenvironmental interpretation

Despite noticeable variability in δ^{34}SCAS among the Clemente marker bed sites, sections from Cerro Rajón exhibit sulfur isotope values that are up to ~8‰ depleted compared to carbonates stratigraphically below (~26‰) and above (~28‰) (see Fig. 5 in Loyd et al., 2012). These decreased isotopic values and an increase in [CAS] of ~1000 ppm in the most unaltered samples, suggest an increased input of isotopically light sulfate to local (perhaps regional) seawater. The ultimate extent of the sulfate increase is poorly constrained; however, given the broad similarities between the Clemente marker bed and the Rainstorm carbonates of Death Valley, ~800 km of Neoproterozoic shelf could have impacted. In addition, δ^{34}SCAS and δ^{13}Ccarb exhibit good positive correlation in both the Clemente and Rainstorm marker beds (Fig. 12) potentially indicative of a common source of sulfate and bicarbonate.

The data presented here and those from Death Valley (Kaufman et al., 2007) can be explained by a transient oxygenation event (see Fig. 13). The transient oxygenation interpretation differs from others concerning the W–S anomaly, which generally involve a rapid global increase in pO2 to near-modern levels that are more or less sustained through the remainder of Earth history (Canfield et al., 2007; Fike et al., 2006; McFadden et al., 2008; Rothman et al., 2003). Whereas the sulfur isotope trends differ significantly between pre- and post-W–S units in Oman (Fike et al., 2006), all of the other analyzed study sites exhibit post excursion trends (and/or variability)
that are indistinguishable from those of the earlier Neoproterozoic
(Kaufman et al., 2007; Loyd et al., 2012; McFadden et al., 2008).
These characteristics imply differential behavior among basins,
with most displaying trends consistent with a transient oxygenation
event(s). The trends of Sonora and Death Valley are discussed
in more detail below.

It is difficult to identify the particular oxidant(s) responsible for
oxygenation; however potential possibilities include free oxygen,
nitrate and/or metal oxides. Given the uncertainties associated
with the distribution of reduced species prior to the onset of this event, it
is impossible (with the present data) to distinguish whether oxidation
affected reduced sulfides and carbon (probably organic matter)
located in (1) marine sediments, (2) the water column (similar to
the deep dissolved organic carbon reservoir of Rothman et al., 2003)
and/or (3) exposed sediments on land (as proposed by Kaufman
et al., 2007). Regardless of the exact initial location of reduced
species, oxidants could react with sulfides and organic carbon and
yield their respective oxidized counterparts SO$_4^{2-}$ and HCO$_3^-$. Due
to the isotopic nature of the reduced parent species, the resultant
oxidized phases would also be isotopically depleted, as there is
no significant fractionation associated with oxidation. In addition,
the residual pyrite and organic carbon contents could be low in
the sediments, particularly if the oxidant penetrated the sediment
column and/or reacted with dissolved species in the water column,
thereby limiting their delivery to the underlying sediments. Whereas organic carbon contents have not been determined in
Sonora carbonates, pyrite contents are exceedingly low (Table 1),
potentially indicative of shallow sedimentary and/or water column
sulfide oxidation (sample insoluble contents of ∼10–20% suggest
that low iron availability probably did not limit pyrite formation).
Additionally, organic carbon contents from the Death Valley W–S
interval are relatively low and show a sharp decrease in the Johnnie Oolite (Kaufman et al., 2007), which lends further support to the
oxidation hypothesis. Although, it should be noted that the controls
on organic carbon contents are complex and low concentrations
may have been brought on for unrelated reasons, particularly in
rocks of such antiquity.

Finally, given sufficient Ca$^{2+}$, an oxidation-produced increase in
HCO$_3^-$ (or CO$_3^{2-}$) would promote conditions more favorable for
carbonate precipitation and could have led to the development of
extensive oolite deposition and aragonite seafloor fan precipitation.
In fact, simple mass balance dictates that the decrease in δ$^{13}$C$_{carb}$ of
∼10‰ (down to ∼−10‰) would require a nearly two-fold increase
in the marine dissolved inorganic carbon reservoir, provided that
organic carbon with an isotopic composition of ∼−25‰ was the pri-
mary oxidized substrate (and an initial marine δ$^{13}$C of ∼0‰). Such
a vast input of dissolved inorganic carbon could have prompted widespread and rapid carbonate precipitation, although limits on the spatial extent of carbonate precipitation are difficult to constrain at this point.

In order to attribute all of these trends to a transient oxygenation event, specific initial conditions for the Sonora and Death Valley regions are required. In order to develop local perturbations in δ34S_sulfate, the initial sulfate reservoir must have been low (perhaps < 2 mM, Loyd et al., 2012), a condition supported by the relatively low concentrations of CAS, highly variable δ34S_CAS and δ34S_pyrite (Hurtgen et al., 2005; Loyd et al., 2012; McFadden et al., 2008), heterogeneous δ34S_CAS (Hurtgen et al., 2006; Loyd et al., 2012; Lyons et al., 2009, 2012) and low or even negative Δ34S_CAS-pyrite (Ries et al., 2009; Shen et al., 2008, 2010, 2011) in non-W–S Neoproterozoic carbonates. In addition, low sulfate concentrations must have existed prior to and after the oxygenation event by continuous removal via BSR in order to account for a significant decrease in δ34S_sulfate (such as the 8% drop observed here) upon sulfide oxidation (recall that isotopically light pyrite is primarily generated as a byproduct of BSR).

When combined, the data suggest that Death Valley and Sonora experienced similar depositional conditions at ~580 Ma. Both locations were either part of one continuous depositional system or perhaps individual, isolated basins encountering similar processes. Similar depositional conditions are geologically reasonable, given that the much of the western edge of North America was experiencing a similar tectonic transition (from a rifted to a passive margin, Levy et al., 1994). The local deviation in δ34S_CAS in the Clemente marker bed and Rainstorm carbonates can be explained by differences in the degree of oxidation and by local deviations in δ34S_pyrite. Variations in CAS concentrations may likewise reflect differences in the quantity of sulfide oxidized, differences in diagenetic removal and/or complexities associated with sulfide incorporation into the carbonate lattice (e.g., Busenberg and Plummer, 1985). Strong correlation with Fe_carb would suggest at least some influence by diagenetic removal, as discussed above, such that those samples with the highest [CAS] are likely most reflective of the primary environment. Ultimately, the increased CAS concentration, reduced and correlated sulfur and carbon isotopic compositions, absence of pyrite and presence of various high alkali indicators can all be explained by a transient oxygenation event ~580 million years ago. Better age constraints and additional spatial characterization are necessary to further understand the duration and extent of this potential event. At this stage it is unclear how an oxidation event would specifically perturb the ancient Death Valley and Sonora marine systems. Future modeling efforts that couple carbon and sulfur isotope behavior will be instrumental in helping better constrain system inputs and outputs and potentially allow for the quantification of system response times. Here, we argue that the data as a whole are consistent with an oxidation event and therefore provide an associated testable hypothesis.

5.8. Broad implications: global heterogeneity in δ34S_sulfate

Using the W–S excursion as a global tie point, δ34S_CAS records from Oman, South China, Death Valley and Sonora can be directly compared (Fig. 14). The compilation demonstrates that similar to Sonora and Death Valley, the inception and isotopic minimum of the W–S in Oman exhibit decreasing δ34S_CAS values and drastically increasing CAS concentrations (Fike et al., 2006). In contrast, the same interval from S. China exhibits a unique trend (McFadden et al., 2008). Although the general characteristics of δ34S_CAS are similar among most of the excursion facies (Sonora, Death Valley and Oman, see Fig. 14), the lack of agreement in the absolute values of δ34S_CAS beyond anything we can easily attribute to diageneis suggests that the marine realm was heterogeneous with respect to δ34S_sulfate during this time interval. Similar heterogeneity in δ34S_CAS is recorded in coeval, Cambrian-aged rocks from multiple localities, interpreted by Gillet et al. (2011) and Loyd et al. (2012) as evidence for sustained low sulfate conditions. The heterogeneity in δ34S_CAS suggests that models and reconstructions based on singular, inferred global δ34S_sulfate values are somewhat flawed and inconsistent with the observed intra-basinal variations. In addition, it is evident that δ34S_CAS alone cannot be used as a chronostratigraphic correlation tool in Neoproterozoic carbonates even if the signal is interpreted as primary.

The global expression of the W–S excursion remains somewhat perplexing. If attributed to an oxygenation event in the Clemente and Rainstorm carbonates, then are similar interpretations warranted elsewhere? Indeed many hypotheses are centered on oxygenation of at least some portions of the ocean-atmosphere system, a particularly attractive hypothesis given the coincident evolution of macroscopic life (Johnston et al., 2012; Knoll, 1996). However, the precise nature of oxygenation and the sources of the
parent reduced carbon species are highly debated (Canfield et al., 2007; Fike et al., 2006; Kaufman et al., 2007; McFadden et al., 2008; Rothman et al., 2003), as well as the possibility of a diagenetic origin (Bristow and Kennedy, 2008; Derry, 2010; Grotzinger et al., 2011; Knauth and Kennedy, 2009; Swart and Kennedy, 2012). If the W–S is indeed a primary signal, we argue that no singular process needs to account for the global oceans and stress that an input of oxidants is likely to affect many if not all reduced reservoirs to varying degrees. For this reason, alternate basins may exhibit similar carbon isotope but unique (and perhaps delayed as in S. China, McFadden et al., 2008) sulfur isotope behavior and still record an oxygenation event. Indeed, the post-W–S transition to low stratigraphic variability in δ34S in Oman contrasts significantly with the successions of Sonora and Death Valley, which both exhibit post W–S variability of the same magnitude as prior to the excursion (Loyd et al., 2012). It seems that during the W–S interval, multiple (but not all) basins record similar δ34S trends, potentially indicative of an oxygenation-associated increased sulfate reservoir. However, the geochemical differences in post-excision facies suggest that the sulfate increase was transient in some basins and possibly more long-lived in others, reflecting differences in how each basin responds to an input of oxidants. Such local behavior may relieve the requirement of extreme oxidant draw down as a result of whole ocean oxygenation as has been proposed as evidence against a primary W–S origin (Bristow and Kennedy, 2008).

As mentioned above, additional geochemical modeling will help resolve these issues. Regardless of the particular controls of the sulfur isotopic composition of marine sulfate, the hypothesis of a heterogeneous δ34S sulfate Neoproterozoic ocean seems to continuously gain support.

6. Conclusions

A locally extensive, carbonate marker bed of the Clemente Formation, Sonora, Mexico expresses δ13C values down to −10‰, consistent with the globally expressed Wonoka–Shuram (W–S) isotope excursion. This marker bed exhibits high variability in CAS concentration and moderate variability in δ34CAS over ~25 km of lateral distance. Negligible correlation of CAS concentration with Mn/Sr ratios and Fe3+ concentrations in all samples is consistent with removal of CAS during diagenetic recrystallization, and samples exhibiting high [CAS] are likely most reflective of the most primary values. δ34CAS does not show correlation with these traditional proxies for diagenesis, suggesting an alternate source of variability, probably arising from local variations in seawater δ34Sulfate.

As a whole, marker bed sulfur systematics are similar to those from coeval fan-bearing carbonates of the Johnnie Formation, Death Valley, California. Both sites show an increase in CAS concentration and a decrease in δ34CAS and δ13Ccarb compared to overlying and underlying carbonates. These trends, in addition to decreased pyrite and the presence of extensive seafloor precipitates, are consistent with a transient oxygenation event.

The W–S excursion has been recognized in many basins worldwide, and sulfur isotope profiles have been developed from two additional localities in Oman and S. China. Whereas similar trends in δ34CAS and CAS concentration are recognized in some temporally equivalent units, the absolute values of δ34CAS differ, suggesting that: (1) the Neoproterozoic oceans were not globally homogeneous with respect to δ34Sulfate and (2) if the trends represent an oxygenation event, each particular basin reacted somewhat differently. This study highlights the likelihood of global heterogeneity in Neoproterozoic δ34CAS, which must be considered in order to characterize oceanic δ34Sulfate and demonstrates that, unlike δ13Ccarb, δ34CAS cannot be used as a correlation tool by itself.

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