Sustained low marine sulfate concentrations from the Neoproterozoic to the Cambrian: Insights from carbonates of northwestern Mexico and eastern California

Sean J. Loyd, Pedro J. Marenco, James W. Hagadorn, Timothy W. Lyons, Alan J. Kaufman, Francisco Sour-Tovar, Frank A. Corsetti

Abstract

Stratigraphic carbonate-carbon isotope trends are similar for correlative Ediacaran and Cambrian carbonates of Sonora, Mexico, and Death Valley, California. In contrast, the sulfur isotope compositions of both carbonate-associated sulfate (CAS) and pyrite in the two regions exhibit unique trends with high degrees of stratigraphic variability. We have established that the sulfur records are coeval using $\delta^{13}C$ chemostratigraphy and biostratigraphic markers, where present. Over short stratigraphic intervals, $\delta^{34}S_{\text{CAS}}$ variability is consistent with regionally low marine sulfate concentrations during this period. Values of $\Delta^{34}S$ ($\delta^{34}S_{\text{CAS}}-\delta^{34}S_{\text{pyr}}$) range from $-5.8\%$ to $+27.1\%$, and average $+11\%$, consistent with limited net fractionation during bacterial sulfate reduction, which is additional evidence for low sulfate concentrations. Modeling based on these regional sulfur isotope trends suggests sustained low sulfate conditions throughout the Neoproterozoic and well into the Cambrian, with concentrations of $\sim2$ mM or lower.

When all of the available sulfate proxy data from our work and previously published studies are considered, most Neoproterozoic and Cambrian successions exhibit trends consistent with low seawater sulfate. The persistent and complete disagreement in $\delta^{34}S_{\text{Sulfate}}$ among multiple basins was briefly interrupted $\sim580$ million years ago, coincident with the onset of the Wonoka-Shuram carbon isotope anomaly and again near the termination of Series 3 of the Cambrian—characteristics generally unrecognized in older rock units. During these two intervals, similar stratigraphic trends in $\delta^{34}S_{\text{CAS}}$ are recorded globally, whereas absolute values remain distinct among individual basins. However, these periods of broad isotopic trend agreement coincide with large-magnitude sulfur isotope excursions, which also point to low seawater sulfate concentrations. Therefore, although brief intervals of isotopic homogeneity exist, the Neoproterozoic and Cambrian ocean must have been dominated by low sulfate throughout. Ultimately, the recognition of persistently low sulfate well into the Paleozoic raises questions about the relationships between sulfate concentration in seawater and its primary controls, including ocean oxygenation and its influence on metazoan evolution.

1. Introduction

The transition from the late Precambrian into the early Phanerozoic was a critical time in Earth history. During this period, Earth crossed major evolutionary thresholds, including the radiation of complex, multicellular life (Signor and Lipps, 1992; Narbonne et al., 1994; Crimes, 1997; Chen and Zhou, 1997; Narbonne et al., 1994; Crimes, 1997; Chen and Zhou, 1997; Jensen et al., 1998; Conway Morris, 1998; Knoll and Caroll, 1999; Xiao and Laflamme, 2009). Whereas the triggers for the evolution...
of metazoans are controversial (Canfield and Teske, 1996; Butterfield, 1997; Valentine, 2004), it is relatively well-accepted that oxygen concentrations must reach critical concentrations for large organisms to exist (Berkner and Marshall, 1966; Runnegar, 1991; Knoll, 1996). Past and more recent studies (e.g., Canfield and Teske, 1996; Hurtgen et al., 2005, 2006; Shen et al., 2006; Fike et al., 2006; Canfield et al., 2007; Kaufman et al., 2007; Halverson and Hurtgen, 2007; McFadden et al., 2008; Fike and Grotzinger, 2008; Canfield and Farquhar, 2009; Shen et al., 2008, 2010, 2011; Li et al., 2010) have used sulfur isotopes as proxies for ocean oxygenation. The results of these studies have yielded varying specific environmental interpretations; however, many argue for increasing sulfate concentrations as a result of progressive oxygenation of the oceans. ‘Global’ interpretations are often based on data from individual sedimentary basins, which is risky given the possibility of heterogeneous oceans during time intervals prior to the Cenozoic (Paytan et al., 1998, 2004a,b; Lyons and Gill, 2010). A better approach to assessing the concentration of sulfate in the oceans demands consideration of all the available data among multiple sedimentary basins within a comparative framework of regional and global patterns, models for ocean oxygenation and metazoan radiation.

Here, stratigraphic data are presented from Neoproterozoic- to Cambrian-aged carbonates of eastern California and northwestern Mexico (Figs. 1 and 2). Analyses from these two, somewhat distant (~800 km apart), time-equivalent localities allow for a more complete characterization of ocean chemistry across the Precambrian–Cambrian boundary (PCB) and into the Cambrian. When sections from around the globe are considered along with those presented in detail here, a picture of sustained low oceanic sulfate concentration emerges.

2. Geologic context

Neoproterozoic to Cambrian strata exposed near the town of Caborca in Sonora, Mexico, represent predominantly shallow marine carbonate and siliciclastic depositional environments (Stewart et al., 1984) generally no deeper than continental shelf depths. Cerro Rajón, the type section for many of the units of interest, is exposed ~30 km to the southeast of Caborca (Fig. 1). The stratigraphic details, biostratigraphic constraints and other notable features of each depositional unit are outlined in Table 1.
Mixed siliciclastic/carbonate units from the Death Valley region of eastern California (Fig. 2) are broadly equivalent to those of the Sonora region, as discussed in Stewart et al. (1984). The Death Valley succession has been studied in detail (e.g., Wright and Troxel, 1966; Stewart, 1970) and its stratigraphy, biostratigraphy and other notable features are summarized in Table 1.

Stewart et al. (1984) noted lithologic similarities between the Death Valley and Sonora successions and suggested some specific correlations. Most notably, they correlated the Rainstorm Member of the Johnnie Formation in Death Valley with a portion of the Clemente Formation in Sonora using the occurrence of a distinctive oolite marker bed (Fig. 3) and noted the occurrence of several, potentially correlative orthoquartzites somewhat higher in the succession (e.g., the Zabriskie Quartzite in Death Valley and the Proveedora Quartzite in Sonora). The recognition of such distinctive lithologies led Stewart et al. (1984) to surmise that the successions reflected similar depositional histories and were deposited along a common passive margin during the Neoproterozoic and Cambrian. The correlation between the two successions can be further refined using new chemostratigraphic and biostratigraphic data as discussed below. In addition, a more detailed Neoproterozoic to Middle Cambrian δ13Ccarb profile from western North America can be constructed because of the greater abundance of carbonate strata in the Sonora section relative to its Death Valley counterpart.

3. Material and methods

Carbonate samples were collected in stratigraphic context from five Neoproterozoic and Cambrian portions of the Cerro Rajón succession and from two sections of PCB and Cambrian facies in Death Valley (Fig. 2). Previous studies by Hurtgen et al. (2004) and Kaufman et al. (2007) provide data from the Noonday Dolomite and Rainstorm Member carbonates of Death Valley, respectively (Fig. 1). Isotopic compositions, CAS, pyrite and elemental concentrations are given in Supplementary Table 1. A more detailed methods narrative is available in the Supplementary Online Material (SOM).

3.1. Carbonate-associated sulfate and pyrite concentrations

Carbonate-associated sulfate (CAS) was extracted using a method modified from Burdett et al. (1989) and Marenco et al. (2008a, 2008b) (see SOM). CAS is reported in parts per million (ppm) within the carbonate fraction of each sample by correcting for the amount of insoluble material. Duplicate measurements of CAS concentration were within ±15%. Pyrite concentration was determined using the chromium reduction method as described by Canfield et al. (1986) and reported in weight percent (wt%) of the original bulk powder. Replicate analyses agreed within ±15%.

3.2. Elemental concentrations

Concentrations for Mn and Sr were determined by inductively coupled plasma-mass spectrometry following sample digestion and dilution in a 1 M HNO3 solution. Helium was used in the collision cell to minimize interferences. Mn and Sr contents are reported in ppm compared to total carbonate (i.e., corrected for the content of insoluble residue). Replicate analyses of Mn and Sr yielded concentrations within ±30 ppm of reported values (see SOM).
Table 1
Stratigraphic characterization of the Sonora and Death Valley successions. Lithologic abbreviations as follows: qtz = quartzite, lime = limestone, dol = dolostone, congl = conglomerate. Superscripts associate observations with references in the right most column.

<table>
<thead>
<tr>
<th>Form/unit</th>
<th>Apx. age</th>
<th>Dominant lithology</th>
<th>Average thickness (m)</th>
<th>Contact with underlying unit</th>
<th>Biostratigraphic components</th>
<th>Unique/notable features</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sonora Succession</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>El Arpa</td>
<td>1.11 Ga–</td>
<td>Dolostone</td>
<td>~100</td>
<td>Erosional</td>
<td></td>
<td></td>
<td>¹Tops 1.11 Ga Aibo Granite ¹Anderson et al. (1979); ¹Rodrigues-Castaneda (1994)</td>
</tr>
<tr>
<td>Caborca</td>
<td>1.11 Ga–</td>
<td>Dolostone</td>
<td>~100</td>
<td>Conformable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clemente</td>
<td>~580 Ma</td>
<td>Shale, qtz</td>
<td>~200</td>
<td>Conformable</td>
<td>Large δ¹³C excursion (W-S), oolite/crystal fan marker bed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pittiquito</td>
<td>580–548 Ma</td>
<td>Quartzite</td>
<td>~75</td>
<td>Conformable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gamuza</td>
<td>580–548 Ma</td>
<td>Dolostone</td>
<td>~115</td>
<td>Conformable</td>
<td>¹Conical stromatolites (Conophyton)</td>
<td></td>
<td>¹Stewart et al. (1984)</td>
</tr>
<tr>
<td>Papalote</td>
<td>580–548 Ma</td>
<td>Dolostone</td>
<td>~430</td>
<td>Conformable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tecolote</td>
<td>580–548 Ma</td>
<td>Quartzite</td>
<td>~75</td>
<td>Conformable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La Ciénega</td>
<td>~542 Ma</td>
<td>Dol, qtz, shale</td>
<td>~175</td>
<td>Conformable?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Puerto Blanco</td>
<td>~542 Ma</td>
<td>Qtz, shale, lime</td>
<td>~700</td>
<td>Erosional</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Proveedora</td>
<td>&lt; 542 Ma</td>
<td>Quartzite</td>
<td>~200</td>
<td>Gradational</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buelna</td>
<td>&lt; 542 Ma</td>
<td>Limestone</td>
<td>~75</td>
<td>Conformable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cerro Prieto</td>
<td>&lt; 542 Ma</td>
<td>Limestone</td>
<td>~80</td>
<td>Conformable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arrojos</td>
<td>&lt; 542 Ma</td>
<td>Shale, lime</td>
<td>~100</td>
<td>Conformable</td>
<td>¹oncoids (Girvanella)</td>
<td>¹top of unit cut out by Jurassic strata ¹Stewart et al. (1984)</td>
<td></td>
</tr>
<tr>
<td><strong>Death Valley Succession</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Noonday</td>
<td>563–580 Ma</td>
<td>Dolostone</td>
<td>~500</td>
<td>Conformable</td>
<td>Stromatolites</td>
<td>¹Marinoan cap carbonate</td>
<td>¹Corsetti and Kaufman (2003); ¹Zhou et al. (2004); ¹Condon et al. (2005)</td>
</tr>
<tr>
<td>Johnnie</td>
<td>~580 Ma</td>
<td>Shale, lime, dol</td>
<td>~600</td>
<td>¹Conformable/²erosional</td>
<td>Stromatolites</td>
<td>³Large δ¹³C excursion (W-S), oolite/crystal fan marker bed, ¦ ~580 Ma incision</td>
<td>³Stewart (1970); ³Summa (1993); ³Corsetti and Kaufman (2003); ³Stewart (1966); ⁴Pruss et al. (2008); ⁴Christie-Blick and Levy (1989); ⁵Abolins et al. (2000)</td>
</tr>
<tr>
<td>Stirling</td>
<td>580–542 Ma</td>
<td>Quartzite</td>
<td>~600</td>
<td>Erosional</td>
<td>¹Cloudina</td>
<td></td>
<td>¹Hagadorn and Waggoner (2000)</td>
</tr>
<tr>
<td>Wood Canyon</td>
<td>~542 Ma</td>
<td>Shale, dol, congl, qtz</td>
<td>~800</td>
<td>Conformable?</td>
<td>¹T. pedum, ²Swarupanta, ²Ernietta, ³olenellid trilobites, ³Archeocyaths, ³inarticulate brachiopods, ²Salterella</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cabrillo</td>
<td>&lt; 542 Ma</td>
<td>Quartzite</td>
<td>~100</td>
<td>Conformable</td>
<td>¹Skolithos</td>
<td></td>
<td>⁴Large δ¹³C excursion (PCB) ¹Horodyski et al. (1994); ²³⁴Corsetti and Hagadorn (2000); ²²Horodyski (1991); ²²Hagadorn and Waggoner (2000); ²²Stewart (1970); ²²Fritz (1975, 1993); ²²Mount et al. (1991)</td>
</tr>
<tr>
<td>Carrara</td>
<td>&lt; 542 Ma</td>
<td>Limestone, siliciclastic</td>
<td>~500</td>
<td>Gradational</td>
<td>¹Oncois (Girvanella), ¹stromatolites, ²Eokochaspis nodosa (trilobites)</td>
<td>²Lower-Middle Cambrian boundary</td>
<td>²Anderson (1990); ²³Corsetti et al. (2002); ²²Palmer (1971)</td>
</tr>
</tbody>
</table>
3.3. Isotopic analyses

3.3.1. Carbon and oxygen

Carbonate carbon and oxygen isotope ratios were determined using a VG Prism II isotope ratio mass spectrometer (IRMS) at the University of Southern California. Samples were microdrilled from thin section billets following thin section examination under a petrographic microscope to ensure sampling of the most pristine phases (phases lacking noticeable recrystallization or otherwise diagenetic/metamorphic alteration). Reproducibility of these measurements is better than 0.1% for both carbon and oxygen, and the data for both are reported using the standard notation relative to the VPDB standard.

3.3.2. Sulfur

Sulfur isotope data were generated using a ThermoScientific Delta V Plus IRMS at the University of California, Riverside, or a GV IsoPrime IRMS at the University of Maryland at College Park. The Delta V Plus IRMS is interfaced with a Costech Analytical Technologies, Inc., elemental combustion system via a Thermo-scientific CONFLO III. The GV IsoPrime IRMS is interfaced with a Eurovector elemental combustion system. Sulfur isotope values are reported in the standard notation relative to the VCDT standard. Interlaboratory comparisons agreed within ±0.5‰, and replicate analyses from individual labs yielded values consistent within ±0.1‰.

3.4. Sulfur modeling

The sulfur isotope data were modeled using the approach of Kah et al. (2004). The theoretical underpinnings of that model are based on Kurtz et al. (2003) and Kump and Arthur (1999). In short, the model allows quantification of the size of the marine sulfate reservoir based on the magnitude of $\delta^{34}S_{\text{sulfate}}$ variability over discrete time intervals. The model specifics, including the rationale behind assigned values of all of the variables and our sensitivity analyses, are discussed in detail in the SOM.

4. Carbon isotope chemostratigraphy

4.1. Sonora region

Prior to this report, high-resolution carbon isotope chemostratigraphy had not been developed for most units of the Sonora region. We begin by characterizing the Sonoran chemostratigraphy in detail and presenting data from supplemental stratigraphic sections in the area (Fig. 2).
4.1. Cerro Rajón

It is best to begin by characterizing the carbon isotope chemostratigraphy of the Sonora region with δ13C_carb results from the type section at Cerro Rajón (Stewart et al., 1984). The El Arpa and Caborca formations at Cerro Rajón exhibit relatively high stratigraphic variability in δ13C with generally positive values near ~+3‰ and up to +6.6‰. The overlying, carbonate-poor Clemente Formation exhibits a prominent negative excursion that reaches an isotopic nadir of ~9.5‰ within the conspicuous carbonate marker bed (Fig. 3) mentioned above (this excursion is observed in the two sections measured at Cerro Rajón). Carbon isotopes return to positive values up section in the Gamuza Formation, exhibit only moderate variability and cluster near 0‰. The muted stratigraphic variability increase smoothly toward 0‰ through the upper two beds of the Clemente Formation, that variably incises the upper portions of the conglomerate that variably incises the upper portions of the upper portion of the La Ciénega Formation. The muted stratigraphic variability continues through the upper part of the Clemente Formation, Tecolote Quartzite and lower-middle La Ciénega Formation as the values increase smoothly toward 0‰.

Near the middle of the La Ciénega Formation coincident with the first appearance of Cloudina (Sour-Tovar et al., 2007), δ13C_carb values decrease sharply, reach a minimum of ~6.2‰ and then increase progressively up section through the remaining 60 m of the unit. Treptichnus pedum occurs in the basal Puerto Blanco Formation (Sour-Tovar et al., 2007) below an extensive boulder conglomerate that variably incises the upper portions of the La Ciénega Formation. Thin carbonate beds within the lower Puerto Blanco Formation record δ13C_carb values near ~4‰, with a minimum value of ~5.9‰. The first appearance of trilobites is recorded near the middle of the Puerto Blanco Formation (Stewart et al., 1984; Sour-Tovar and Hagadorn, 2010). Further up section, in archeocyathid-bearing limestones, the trend shows moderate variability and somewhat less negative values near ~2‰. Values increase to ~0‰ within the uppermost-sampled carbonate beds of the Puerto Blanco Formation. The Buelna Formation (overlying the carbonate-free Proveedora Quartzite) displays carbon isotope compositions of ~2‰, aside from one outlier of ~6‰. δ13C_carb shifts to much more negative values coincident with the transition into the overlying Cerro Prieto Formation. The values increase through the Cerro Prieto and Arrojos formations and reach a maximum of ~0‰ at the top of the succession.

4.1.2. Cerro El Arpa

The El Arpa Formation at Cerro El Arpa is more than twice as thick as its equivalent at Cerro Rajón (Stewart et al., 1984). δ13C_carb values are extremely positive (~+8‰ on average) throughout most of the formation. Stratigraphic variability in δ13C_carb is relatively high in the lower half of the formation and fairly low in the remainder. Values begin to decrease from ~7.7‰ at a siliciclastic-dominated interval in the middle of the El Arpa Formation and fall to a minimum of ~3.3‰ at the top of the formation.

4.1.3. Cerro Clemente and Cerro Calaveras

Two sections containing the conspicuous carbonate marker beds of the Clemente Formation were sampled at Cerro Clemente and one at Cerro Calaveras (see Figs. 1–3). All three sections exhibit the pronounced negative δ13C_carb excursion recorded in the marker bed interval at Cerro Rajón. At Cerro Clemente, the lowermost horizon of the marker bed displays a δ13C_carb of ~3.4‰ and reaches a value of ~8.8‰ near the top of the sequence. In the higher resolution Cerro Clemente section (Cerro Clemente 1 in Supplementary Table 1), values increase from ~8.8‰ to ~7.1‰ through the remaining 1.3 m of the marker bed. The lowermost sample of marker bed at Cerro Calaveras records a δ13C_carb value of ~4.6‰ and drops to a minimum value of ~8.4‰ before returning to the slightly higher value of ~8.0‰ at the top of the sequence.

4.2. Death Valley

The δ13C_carb data shown in Fig. 2 are compiled from the work of Corsetti (1989), Hurtgen et al. (2004) (Noonday Dolomite), Corsetti and Kaufman (2003), Kaufman et al. (2007) (Johnnie Formation) and this study (Wood Canyon and Carrara Formations). Our new δ13C_carb data from the Wood Canyon Formation agree well with those reported previously by Corsetti and Hagadorn (2000, 2003). Data generated by re-sampling the three prominent carbonate beds in the lower Wood Canyon Formation are indistinguishable from previous work and show an up section decrease (down to ~4‰ in the lowermost bed followed by an increase in the upper two beds to values near 0‰ (Fig. 2). The two data points from the upper Wood Canyon occur significantly higher in the section and yield values near ~6‰. Data from the Carrara Formation oscillate between ~2‰ and ~2‰.

4.3. Integrity of δ13C_carb chemostratigraphy

Because carbonates tend to recrystallize in post-depositional settings, it is important to address diagenetic overprinting. When all the data are viewed together, there is no significant covariation between δ13C_carb and δ18O_carb (Fig. 4A) (such covariation is often taken as a fingerprint of diagenesis). However, as has been recognized in many δ13C_carb excursion-containing units of Neoproterozoic age, a positive correlation exists between δ13C_carb and δ18O_carb when the excursion facies are examined individually (Fig. 4B) (Derry, 2010). Similar covariation in other Neoproterozoic units has been hypothesized by Knauth and Kennedy (2009) to represent meteoric diageneisis, a process that can reset both δ13C_carb and δ18O_carb to values lower than primary marine carbonates (Allan and Mathews, 1982; Banner and Hanson, 1990). The ‘meteoric hypothesis’ can be tested through independent analyses such as the concentrations of strontium and manganese—elements that are partitioned differently in meteoric and marine fluids—with marine waters being relatively enriched in Sr and depleted in Mn compared to meteoric waters (Bodine et al., 1965; Kinsman, 1969; Brand and Veizer, 1980). Carbonates experiencing recrystallization by meteoric fluids are predicted to exhibit positive correlations for Sr versus δ13C_carb and δ18O_carb; negative correlations are predicted between δ13C_carb and δ18O_carb versus Mn/Sr. Such correlations are not seen in the data from the Sonora locales (Fig. 4C, D), evidence that these units likely did not experience significant meteoric diageneisis, despite a positive correlation between δ13C_carb and δ18O_carb. The conflicting implications of these data are perplexing and much is yet to be learned concerning the nature of this positive isotope correlation; however, as discussed below, unraveling this problem is not necessary for the purposes of this study.

Meteoric alteration is not the only diageneric mechanism that can overprint carbonate chemistry, and burial alteration has also been proposed as a δ13C_carb excursion-producing process (Derry, 2010). Unlike meteoric diageneisis, deeper burial processes can occur under conditions far-removed from those exhibited by typical surficial fluids and therefore impart wide-ranging, often unpredictable geochemical signatures in carbonates. Regardless of the source of the carbon isotope values in Neoproterozoic carbonates (even if from burial or other diageneric pathway), the striking global similarity in δ13C_carb trends are testament to their retained utility as a chemostratigraphic tool (see recent review by Grotzinger et al., 2011). Therefore, we use the δ13C_carb data from
Death Valley and Sonora in the traditional stratigraphic way, and specifically use marked excursions (such as the W-S and PCB excursions) as correlation tie points. These tie points are bounded by regionally extensive, mappable sequence boundaries and/or unusual lithofacies (Hagadorn, 2011).

4.4. Correlation between Sonora, Death Valley and beyond

It is not currently known how units older than the Clemente Formation correlate with those predating the Rainstorm Member of the Johnnie Formation. The Sonora succession lacks glacial and associated cap carbonate deposits characteristic of Neoproterozoic sections worldwide, yet these features occur in the Death Valley Succession. The El Arpa Formation contains the most positive $\delta^{13}C_{\text{carb}}$ values in the Sonora succession, with some values approaching $+10\%o$. No carbonates in the Death Valley Succession have such enriched values. In the absence of other stratigraphic indicators, any attempt to correlate the $\delta^{13}C$ data from this interval among the regions is equivocal. It is equally parsimonious to correlate the El Arpa/Caborca formations with the Beck Spring Dolomite (with $\delta^{13}C_{\text{carb}}$ values of up to $+5\%o$; Corsetti and Kaufman, 2003), the ‘unnamed limestone’ of the Kingston Peak Formation (with $\delta^{13}C_{\text{carb}}$ reaching $+5\%o$; Prave, 1999) or the pre-Rainstorm Member portion of the Johnnie Formation (with $\delta^{13}C_{\text{carb}}$ of $+3.5\%o$; Corsetti and Kaufman, 2003; Verdel et al., 2011). It is also possible that there are no Death Valley strata that are time equivalent to the El Arpa/Caborca formations, and in the absence of additional information, the correlations remain uncertain.

Although the Death Valley Succession does not record $\delta^{13}C_{\text{carb}}$ values approaching $+10\%o$, the Neoproterozoic succession near Pocatello, Idaho, does. Thin dolostones from the Caddy Canyon Quartzite yield $\delta^{13}C_{\text{carb}}$ values above $+9\%o$. The Caddy Canyon Formation is constrained radiometrically to be between $\sim 667$ and $\sim 580$ million years old (Christie-Blick and Levy, 1989; Fanning and Link, 2004). The global $\delta^{13}C_{\text{carb}}$ compilation of Halverson et al. (2005) contains two intervals between 667 Ma and 580 Ma that record $\delta^{13}C_{\text{carb}}$ in excess of $+8\%o$, one lying between the Sturtian and Marinoan glaciations and the other postdating the Marinoan Glaciation (although Kaufman et al., 2009, suggest that the younger interval may also be pre-Marinoan in age). It is possible that the El Arpa/Caborca formations correlate with these intervals, but again, precise correlation is equivocal.

In contrast to the El Arpa and Caborca formations, the overlying units of Cerro Rajo´n correlate well with those of Death Valley via litho-, chemo- and biostratigraphy and are consistent with correlations proposed previously (Stewart et al., 1984). Stewart et al. (1984) suggested that the Clemente Formation correlates with the Johnnie Formation largely on the basis of similar lithology, including the prominent oolitic marker bed found in both successions; a correlation now supported by our $\delta^{13}C_{\text{carb}}$ data. The marker bed carbonates in both successions record a striking negative anomaly (Fig. 2). In Death Valley, the negative $\delta^{13}C_{\text{carb}}$ anomaly has been correlated to the Wonoka-Shuram (W-S) anomaly (Corsetti and Kaufman, 2003; Verdel...
Fig. 5. Chemostratigraphic trends of Cerro Rajón, Sonora, Mexico.

Fig. 6. Chemostratigraphic trends of the Death Valley Succession, eastern California, USA (early and mid-Ediacaran data from Hurtgen et al., 2004 and Kaufman et al., 2007, respectively).
et al., 2011), and we agree with this correlation for both Death Valley and Sonora (the inception of the W-S anomaly is dated at \(~580\) Ma from units in Oman, Bowring et al., 2003). The lower Wood Canyon and the La Ciénega/lowermost Puerto Blanco formations correlate well and bracket the PCB. Both units exhibit a negative \(\delta^{13}C_{\text{carb}}\) excursion, characteristic of the PCB around the world. The isotopic nadir is bounded below by the occurrence of Cloudina (Hagadorn and Waggoner, 2000; Sour-Tovar et al., 2007), and it is interesting to note that Cloudina occurs in association with the inception of the negative excursion. Elsewhere (e.g., Namibia, Grotzinger et al., 1995), Cloudina occurs prior to the excursion, thus the Sonora succession likely records the youngest currently recognized occurrence of Cloudina.

The PCB-delineating trace fossil Treptichnus pedum appears in overlying units of the Puerto Blanco Formation (Fig. 2) (Sour-Tovar et al., 2007). Ultimately, the PCB is strictly dictated by the first occurrence of T. pedum, however due to the facies dependency of this organism (T. pedum is only found in siliciclastic rocks, Corsetti and Hagadorn, 2000) as well as traditional issues with trace fossil preservation, we place the PCB a bit lower in the section, coincident with the \(\delta^{13}C\) excursion (see Fig. 2). An erosional unconformity occurs above T. pedum at each locality and cuts out portions of the lowermost Puerto Blanco Formation and the lower Wood Canyon Formation. The lowest occurrences of trilobites, brachiopods and echinoderms occur near the middle of both the Puerto Blanco and Wood Canyon formations (Stewart, 1970; Stewart et al., 1984; Sour-Tovar and Hagadorn, 2010), suggesting further correlation between the regions. It should be noted that some suggest that the Death Valley and Sonoran successions were located much more proximally to one another and that their present spatial separation resulted from Mesozoic offset along the so-called “Sonora-Mojave Megashear”, a large yet now cryptic strike-slip fault system. The hypothesis has its supporters (Anderson and Schmidt, 1983; Anderson and Silver, 2005; Nourse et al., 2005; Stewart, 2005) and detractors (Poole et al., 2005; Stevens et al., 2005; Iriondo et al., 2005; Amato et al., 2009); however, the specific spatial distribution of these two successions does not have bearing on the conclusions we reach here.

### 5. Sulfur isotopes

\(\delta^{34}S_{\text{CAS}}\) values exhibit high stratigraphic variability in both successions (Figs. 5 and 6). Isotopic swings of \(~10\)% in less than 100 m of section are relatively common. The ranges in isotopic values span from \(-1.5 \) to \(+31.6\)\% in Sonora and \(+11.0 \) to \(+37.3\)\% in Death Valley. When small-scale variability is ignored, both sections display sulfur isotope values oscillating around a mean similar to the composition of modern seawater sulfate (\(~+21\)%) (Rees et al., 1978). Specifically, average \(\delta^{34}S_{\text{CAS}}\) values are \(+21.6\) and \(+22.5\)% in Sonora and Death Valley, respectively. \(\delta^{34}S_{\text{pyr}}\) values also display high stratigraphic variability, with values from Sonora ranging from \(-12.2\)% to \(+30.5\)% and averaging \(+13.3\)\%. Samples from Death Valley exhibit \(\delta^{34}S_{\text{pyr}}\) values that range from \(+2.9\)% to \(+30\)% and average \(+15.6\)%.

The relative enrichment in \(34\)S between contemporaneous \(\delta^{34}S_{\text{CAS}}\) and \(\delta^{34}S_{\text{pyr}}\) is denoted by \(\Delta^{34}S\), where \(\Delta^{34}S = \delta^{34}S_{\text{CAS}} - \delta^{34}S_{\text{pyr}}\). All but

![Fig. 7. Transposed plots of the Sonora and Death Valley \(\delta^{34}S_{\text{CAS}}, \delta^{34}S_{\text{pyr}}, \) and \(\Delta^{34}S\) data. Notice how the \(\delta^{34}S_{\text{CAS}}\) and \(\delta^{34}S_{\text{pyr}}\) trends exhibit high variability. Data points plotted based on correlation via \(\delta^{13}C_{\text{pyrr}}\). Neoproterozoic and Cambrian \(\delta^{13}C_{\text{carb}}\) from Fike et al. (2006) and Zhu et al. (2006), respectively. CAS and \(\delta^{34}S_{\text{CAS}}\) data of Death Valley from Hurgen et al. (2004), Kaufman et al. (2007) and this study. Radiometric dates obtained by comparing \(\delta^{13}C_{\text{carb}}\) to alternate localities including Oman [O] (Fike et al., 2006), South China [S, SC] (McFadden et al., 2008) and Morocco [M] (Maloof et al., 2005). Time-scale-\(\delta^{13}C_{\text{carb}}\) correlation as presented in Ogg et al. (2008).](image-url)
one of the $\Delta^{34}S$ values for Sonora carbonates fall between −5.8‰ and +27.1‰ and average +10.5‰ (the one value of −22.9‰ is considered an outlier and was removed from the average). Death Valley carbonates show a $\Delta^{34}S$ range from +2.0‰ to +22.4‰ and an average of +12.9‰. More generally, the carbonates from both regions reveal highly variable $\Delta^{34}S$ values (Fig. 7).

6. Interpreting the sulfur record

6.1. CAS concentration

Modern carbonates precipitated from normal seawater record CAS concentrations between ~1000 and 4500 ppm and average ~2400 ppm (Lyons et al., 2004; Gellatly and Lyons, 2005). However, the incorporation of CAS into the carbonate lattice is not well understood and may be dependent on mineralogy (Gill et al., 2008; Marenco et al., 2008b) and crystallization rate (Busenberg and Plummer, 1985). Biogenic carbonates typically incorporate more CAS relative to abiotic precipitates and show wide variability among taxonomic groups (Mekhtiyeva, 1974; Burdett et al., 1989; Staudt and Schoonen, 1995). Also, aragonite incorporates significantly more CAS than calcite (Gill et al., 2008). Meteoric diagenesis is known to remove CAS, while leaving the Cenozoic ocean is relatively invariant (Paytan et al., 1998, 2008; Marenco et al., 2008b) and crystallization rate. However, the incorporation of CAS into the carbonate lattice is not well understood and may be dependent on mineralogy (Gill et al., 2008; Marenco et al., 2008b) and crystallization rate (Busenberg and Plummer, 1985). Biogenic carbonates typically incorporate more CAS relative to abiotic precipitates and show wide variability among taxonomic groups (Mekhtiyeva, 1974; Burdett et al., 1989; Staudt and Schoonen, 1995). Also, aragonite incorporates significantly more CAS than calcite (Gill et al., 2008).

6.2. Sulfur isotopes and marine sulfate

The $\delta^{34}S$ values of CAS and coeval pyrite offer another window into the Ediacaran–Cambrian sulfur cycle—one that is perhaps less vulnerable to diagenetic overprints and differences in primary uptake (e.g., vital effects) compared to CAS concentrations. That said, $\delta^{34}S_{\text{CAS}}$ values may be contaminated by pyrite oxidation during sample analysis (Marenco et al., 2008a; Mazumdar et al., 2008). Fortunately, such contamination should produce a negative correlation between $\delta^{34}S_{\text{CAS}}$ and the concentration of pyrite (expressed in the molar ratio of pyrite:CAS in Supplementary Figure 1) because pyrite, in general, is relatively $34$S-depleted compared to sulfate in the same sample as a result of fractionations during bacterial sulfate reduction. Supplementary Figure 1 demonstrates that no such correlation exists, suggesting that the data presented here are not contaminated by pyrite oxidation via weathering or during CAS extraction.

6.2.1. High stratigraphic variability in $\delta^{34}S_{\text{CAS}}$

If tracking primary seawater trends, high variability in $\delta^{34}S_{\text{CAS}}$ is indicative of low sulfate concentrations (Kah et al., 2004; Hurtgen et al., 2005). We see such a relationship in the Sonora and Death Valley successions. In contrast, $\delta^{34}S_{\text{sulfate}}$ in the Cenozoic ocean is relatively invariant (Paytan et al., 1998, 2004a,b), largely because of the high concentration (~28 mM) and long residence time (10^7 yr) of sulfate in recent seawater. Isotopic mass balance dictates that large changes in the $\delta^{34}S$ of seawater sulfate can only occur if the sulfate concentration is low and thus easy to perturb. The high stratigraphic variability presented here thus points to low oceanic sulfate during the Neoproterozoic, and these low concentrations persisted well into the Cambrian. We address how low these concentrations may have been using a simple box model in Section 6.2.3.

6.2.2. $\Delta^{34}S$

Despite the risk of oversimplification, $\Delta^{34}S$ values (defined above as $\delta^{34}S_{\text{CAS}}-\delta^{34}S_{\text{pyr}}$) are commonly assumed to represent the isotopic separation between source fluid sulfate and the microbially produced hydrogen sulfide. The magnitude of this separation is partially dependent on the sulfate concentration; bacterial sulfate reduction and associated disproportionation reactions yield higher fractionation in fluids with adequate sulfate (Harrison and Thode, 1958; Canfield, 2001; Habicht et al., 2002; Canfield et al., 2010). Habicht et al. (2002) found highly suppressed fractionation approaching 0‰ at sulfate levels below ~200 µM (<1% of the modern level); however, at sulfate concentrations above 200 µM, instantaneous and net fractionations were shown to vary widely, even under relatively low sulfate concentrations. Fractionations of ~20–50‰ can be achieved in fluids with sulfate contents between 0.2 and 1 mM (Canfield, 2001; Habicht and Canfield, 2001; Farquhar et al., 2008). Canfield et al. (2010) demonstrated that even at sulfate concentrations between 1.2 and 2 mM, fractionations as much as 70‰ can be expressed. Ultimately, relatively low $\Delta^{34}S$ values, such as those recognized here (averaging ~11‰), can be reasonably attributed to low sulfate conditions in agreement with the high stratigraphic variability in $\delta^{34}S_{\text{CAS}}$. The wide variability in $\Delta^{34}S$ recognized in past studies is partially a product of alternate controls (e.g., the specific type of sulfur metabolism; Canfield and Teske, 1996), and therefore direct calculation of sulfate concentrations via $\Delta^{34}S$ is precluded. However, the ~11‰ average $\Delta^{34}S$ values of Death Valley and Sonora are consistent with low sulfate concentrations (similar to those inferred by Gill et al., 2011).

6.2.3. Modeling marine sulfate from the Neoproterozoic to the Cambrian

Because of challenges presented to interpretations of sulfate concentrations based only on fractionations between sulfate and sulfide, additional perspectives are required. The sulfate sulfur isotopic composition of the oceans is susceptible to change due to distinct differences in the isotopic compositions of the primary inputs and outputs of sulfur to the ocean (Garrels and Lerman, 1984). The rate at which the isotopic composition can change is inversely proportional to the size of the reservoir (Kurtz et al., 2003; Kah et al., 2004) as is evident in the following equation:

$$d\delta_{\text{CAS}}dt = [F_w(\delta_{\text{w}} - \delta_{\text{CAS}}) - F_{\text{pyr}}\Delta S]/M_{\text{O}}$$

(1)

where $d\delta_{\text{CAS}}/dt$ is the change in the sulfur isotope composition of oceanic sulfate over a given time in units of ‰/Myr, $F_w$ is the total flux of sulfur entering the oceans as sulfate in mol/Myr with the isotopic composition $\delta_w$ in ‰, $F_{\text{pyr}}$ is the flux of sulfur leaving the oceans as pyrite in mol/Myr, $\Delta S$ is the difference between the isotopic composition of coeval sulfide and sulfate (thus values are typically negative), and $M_O$ is the mass of sulfate in the oceans. Note that the other primary sink for sulfur in the oceans, evaporite deposition, does not appear in the above equation because evaporite precipitation imparts only a very small fractionation relative to contemporaneous seawater sulfate (evaporates are enriched in $\delta^{34}S$ by only ~2.4‰ (Ault and Kulp, 1959; Raab and Spiro, 1991) and thus evaporite deposition would not significantly alter the isotopic composition of seawater sulfate).

Most of the variables correspond to those used in previous studies using a similar modeling approach (see Supplementary Tables 2 and 3). $F_w$ and $\delta_w$ are considered to be equal to the modern values of $1.5 \times 10^{18}$ mol/Myr and +8‰, respectively, $F_{\text{pyr}}$ is assigned values of $6.7 \times 10^{17}$, $1.0 \times 10^{18}$ and $1.5 \times 10^{18}$ mol/Myr, corresponding to those previously inferred as the Phanerozoic average (Kurtz et al., 2003), the Cambrian SPICE interval (Gill et al., 2011) and the Neoproterozoic average (Canfield and...
Values of \(d_{O}/dt\) and \(d_{O}\) are taken directly from our data, where \(d_{O}\) is considered equivalent to \(d_{34}S_{CAS}\), and \(d_{O}/dt\) is calculated as explained in the SOM. The specific isotopic shifts (or excursions) in \(d_{34}S_{CAS}\) modeled here are labeled in Fig. 8. The sensitivity of the model to select parameters is explored in the SOM (see Supplementary Figures 2 and 3).

Of the above variables, the \(F_{pyr}\) value of 1.0 \(\times 10^{18}\) mol/Myr and a \(\delta_{pyr}\) value of +8\% produce consistently plausible results (\(M_{O}\) consistently > 0, see SOM). As predicted, the model yields dominantly low sulfate concentrations, with values of ~2 mM or less and a solitary high value of ~11 mM (Fig. 8). On average (considering variability in deposition rate, see SOM), reconstructed sulfate concentrations are ~1.4 mM and similar in Sonora (avg. ~2 mM) and Death Valley (avg. ~0.8 mM). As an additional test, model runs involving marine sulfate concentrations of the modern ocean (28 mM) are explored in the SOM. The results of this model demonstrate that the isotopic swings recorded in these data could not have been generated in oceans with such high sulfate concentrations (Supplementary Figure 4). Although the model produces significant temporal variability in reconstructed sulfate concentrations, its simplicity and the potential problems associated with predicting certain model parameters make detailed interpretations speculative. Despite the intrinsic challenges, this model supports the overall hypothesis of low, likely very low, sulfate concentrations in the ocean.

6.3. The evolving marine sulfate reservoir

While many consider the post-glacial Neoproterozoic to be a time of transition with regard to oceanic sulfate—specifically marked by an increase in concentration—the timing of the ultimate sulfate rise is debated. The Sonora and Death Valley data indicate relatively low (at least regionally) concentrations spanning from the Neoproterozoic to Series 3 of the Cambrian (Fig. 8). The generally elevated CAS concentrations in Cambrian rocks of Sonora and Death Valley likely reflect influences on CAS incorporation and/or preservation that are not related to initial sulfate conditions—perhaps cryptic diagenesis or uptake controlled by precipitation rate and/or mineralogy, for example. Ultimately, the controls dictating absolute CAS concentrations remain poorly understood, particularly in old sedimentary carbonates.

6.3.1. Additional \(\Delta^{34}S\) records

Multiple localities exhibit increased \(\Delta^{34}S\) in the terminal Neoproterozoic, including Oman (Fike et al., 2006), south China (McFadden et al., 2008), Namibia and Australia (Hurtgen et al., 2005; Halverson and Hurtgen, 2007). However, these increases vary in their stratigraphic profiles (stepwise in S. China versus monotonic in Oman) or are poorly characterized because of a paucity of data (Namibia and Australia). In addition, the magnitudes of the \(\Delta^{34}S\) increases vary from +10\%w (a jump from ~ +11 to +21\%w) in S. China (McFadden et al., 2008) to +50\%w (from ~0 to +50\%w) in Oman (Fike et al., 2006). The increases recognized in these localities may reflect locally increased sulfate concentrations or controls on \(\Delta^{34}S\) other than sulfate abundance. Canfield et al. (2007) and Shen et al. (2006) projected increasing \(\Delta^{34}S\) by comparing \(\delta_{pyr}\) values to an assumed global ocean value for \(\delta_{pyr}\); however, the growing body of \(\delta_{pyr}\) data (from CAS and evaporite minerals) suggests that Neoproterozoic oceans did not exhibit a singular \(\delta_{pyr}\) value. Ultimately, rising \(\Delta^{34}S\) values in
the Ediacaran can be explained without high or rising sulfate concentrations and in fact, the comparative variability among sites is more parsimonious with overall low sulfate conditions, perhaps comparable to the earlier Proterozoic.

Further evidence for overall low sulfate conditions during the Neoproterozoic is the recurrence of negative $\delta^{34}S$ values in some localities (Shen et al., 2008, 2010, 2011; Ries et al., 2009). Although the mechanisms required to produce $\delta^{34}S_{\text{Pyr}} > \delta^{34}S_{\text{CAS}}$ are poorly understood and difficult to rationalize on a broad scale, all of them require low sulfate conditions.

6.3.2. Fluid inclusions data
Evidence for high sulfate ‘snapshots’ in the latest Neoproterozoic ($\sim$545 Ma) lies with fluid inclusion data from contemporaneous deposits in Oman (Horita et al., 2002) and Pakistan (Kovalevych et al., 2006). The chemical compositions of fluid inclusions within recrystallized halite from Pakistan suggest a sulfate-rich, likely seawater source. However, as Kovalevych et al. (2006) stress, the absolute concentration of seawater sulfate cannot be calculated directly from these secondary inclusions, and the original fluid can only be characterized as sulfate- versus calcium-rich—thus leaving a significant margin of error in the estimates of sulfate concentration. Fluid inclusions from the Ara Formation in Oman have been used to reconstruct seawater sulfate contents of $\sim$17–23 mM (Horita et al., 2002), levels that were not likely reached again until the late Paleozoic to early Mesozoic (Lowenstein et al., 2003). As noted by Ries et al. (2009, online information), the sulfate concentrations of $\sim$20 mM (Horita et al., 2002) are extrapolated by adding the actual $\sim$6 mM fluid inclusion sulfate concentration to a significant amount proposed to have been lost during subsequent CaSO$_4$ precipitation. Therefore without better constraints on this loss component, the fluid inclusion data from Oman remain vulnerable to other interpretations.

Ignoring the potential pitfalls involved with reconstructing seawater chemistry from fluid inclusion data, the two accounts of high sulfate from Pakistan and Oman may simply reflect local, high
sulfate conditions. Indeed, as our understanding of sulfate evolution in the Neoproterozoic expands, the notion of a heterogeneous ocean that was either vertically stratified (Shen et al., 2008, 2010, 2011; Ries et al., 2009; Lyons et al., 2009; Li et al., 2010; Xiao et al., 2012) or laterally variable (this study; Lyons and Gill, 2010; Lyons et al., 2009, 2012) seems to be the most parsimonious interpretation, at least with respect to sulfate and $\delta^{34}S_{\text{Sulfate}}$. Such heterogeneities are possible, and indeed favored, when oceanic sulfate concentrations are low and the residence times correspondingly short.

6.3.3. Sulfate concentration in the earliest Cambrian

Modeling by Canfield and Farquhar (2009) suggests that sulfate concentrations may have risen (up to $\sim$10 mM or more) in the earliest Cambrian as a result of sedimentary sulfate oxidation by bioturbating organisms. In their model, sulfate concentrations are projected from the isotope mass balance-derived proportions of sulfur buried as pyrite and evaporate phases. Intuitively, an increase in the fraction of sulfur buried as sulfate evaporites (or decrease in the fraction buried as pyrite) is taken to represent an increase in marine sulfate concentrations. They calculate the proportion of sulfur buried as pyrite (or ‘f-ratio’) from $\sim$3.0 Ga to the modern and show that a pronounced decrease is initiated at approximately the same time as the PCB. However, the fairly rapid jump in sulfate concentration across the PCB inferred by their model does not exhibit a profile similar to the calculated fractional burial of pyrite. Instead, the f-ratio decreases quasi-linearly until it reaches a minimum value of $\sim$0.5 about 200 million years after the PCB. This $\sim$0.5 value is apparently sustained throughout the remaining Phanerozoic (see Fig. 1 in Canfield and Farquhar, 2009). Perhaps the much slower decrease in the fractional burial of pyrite more closely reflects the sulfate content of the oceans, rather than the model projection. Indeed, this would be more parsimonious with the data presented here and elsewhere (Hurtgen et al. 2009; Gill et al., 2011), which indicate low sulfate concentrations ($<\sim$2 mM) throughout the Cambrian.

Finally, Canfield and Farquhar (2009) apply a uniform $\delta^{34}S_{\text{Sulfate}}$ value among sedimentary basins. The increasing likelihood of a heterogeneous ocean, however, suggests that application of any one $\delta^{34}S_{\text{Sulfate}}$ value beyond the individual basin from which it was derived is unwarranted. Therefore, their absolute f-ratios and the subsequent inferences on global sulfate concentrations are somewhat suspect.

Whereas bioturbation likely led to a relative increase in sedimentary sulfate oxidation in the Cambrian and early Paleozoic, its quantitative influence on absolute sulfate concentrations has yet to be established (see also concerns raised in commentary by Lyons and Gill, 2010), particularly in a global context. In all likelihood, the abundance of residual reduced compounds (i.e., organic matter, iron (II), etc.) could have remained high in the oceans for much of the early Paleozoic, a relic of an environment that experienced $\sim$4 billion years of reducing conditions. Any initial sulfate produced by sedimentary sulfate oxidation (fueled by the onset of bioturbation) could have been consumed by subsequent reducing reactions, suppressing an immediate buildup of sulfate.

6.3.4. A persistently low sulfate ocean

We hope to have demonstrated the likelihood that low marine sulfate concentrations (probably $\sim$2 mM or lower) persisted well into Series 3 of the Cambrian (Fig. 8). Gill et al. (2011) argued that the late Cambrian SPICE interval also exhibited relatively low sulfate oceans based on sulfur isotope proxies. In contrast to our study, the SPICE interval exhibits generally similar trends in $\delta^{34}S_{\text{CAS}}$ and $\delta^{34}S_{\text{pyr}}$ among four basins worldwide (albeit absolute values are distinct among basins, as noted by Gill et al., 2011). However, the SPICE records depict a large-magnitude sulfur isotope excursion that could not have been generated unless sulfate concentrations were quite low. In fact, the sulfate concentration required to reconstruct the sulfur excursions ($\sim$1.5 mM) overlaps with the model data presented here. The data of Hurtgen et al. (2009) from a coeval SPICE interval in Newfoundland show a $\delta^{34}S$ trend distinct from those of Gill et al. (2011) and exhibit relatively high stratigraphic variability. Ultimately, the general isotopic trend similarity among four out of five basins is intriguing, but in this case necessitates persistently low sulfate conditions.

When all of the available sulfate proxy data from globally distributed Neoproterozoic and Cambrian deposits are considered together, the idea of an overall persistently low sulfate ocean is bolstered (see Supplementary Figure 5 for a paleogeographic reconstruction). As seen in Fig. 9, most sections exhibit geochemical data that are consistent with low sulfate. In Fig. 9, basins with low variability in $\delta^{34}S_{\text{CAS}}$, smooth stratigraphic trends in $\delta^{34}S_{\text{CAS}}$ and very high CAS concentrations are interpreted as having elevated sulfate concentrations. Proposed low sulfate basins are those with high variability in $\delta^{34}S_{\text{CAS}}$ and very low or negative $\Delta^{34}S$ values. Because of the challenges in interpreting $\Delta^{34}S$ values in general (and negative $\Delta^{34}S$ values in particular), these data are not straightforwardly translated into sulfate concentrations and thus are left out of the reconstruction in Fig. 9. Ultimately, Fig. 9 suggests that low sulfate conditions dominated throughout most of the Ediacaran and Cambrian.

7. Conclusions

Temporally equivalent carbonates from Death Valley and Sonora express $\delta^{34}S_{\text{CAS}}$ values with high stratigraphic variability and lack agreement between the two locations. $\Delta^{34}S$ values are consistently below 28‰ and average 11‰, similar to earlier Proterozoic successions. The variability in $\delta^{34}S_{\text{CAS}}$, differing regional trends and low $\Delta^{34}S$ values are consistent with the persistence of relatively low sulfate conditions well into Series 3 of the Cambrian. Simple box modeling suggests that these concentrations were quite low (probably $\sim$2 mM or lower) compared to modern values.

Additional evidence for low Neoproterozoic sulfate involves a lack of agreement among multiple, similarly aged basins worldwide. These disagreements have spawned the idea of heterogeneous oceanic $\delta^{34}S_{\text{Sulfate}}$, a state that is unlikely to persist in an ocean with high sulfate content. Individually, most basins throughout the Neoproterozoic and Cambrian exhibit trends consistent with low sulfate. When considered together within a multi-basin framework, this entire interval is characterized by low sulfate. These findings raise questions concerning a simple connection between sulfate and rising oxygen concentrations and links to metazoan evolution.

Acknowledgments

We would like to thank Will Berelson, Dave Bottjer, Ben Gill, Doug Hammond, Stew Hollingsworth, Katherine Mareno, Victoria Petryshyn and Jack Stewart for insightful scientific discussion. Mathew Hurtgen, one anonymous reviewer and AE Gideon Henderson provided insightful and constructive reviews. Steven Bates, Miguel Roncin and Lowell Stott are acknowledged for assistance with analyses. Funding was provided to SJL, PJM, AJK and FAC by NSF and TWL by the NASA Exobiology Program. SJL is partially supported by the Agouron Institute Geobiology Postdoctoral Fellowship.


