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

Sean J. Loyd [a,b,*], Pedro J. Marenco [c], James W. Hagadorn [d], Timothy W. Lyons [e], Alan J. Kaufman [f], Francisco Sour-Tovar [g], Frank A. Corsetti [b]

[a] Department of Earth and Space Sciences, University of California, Los Angeles, 595 Charles Young Drive East, Los Angeles, CA 90095, USA
[b] Department of Earth Sciences, University of Southern California, 3651 Trousdale Avenue, Los Angeles, CA 90089, USA
[c] Department of Geology, Bryn Mawr College, 190 Park Science Building, Bryn Mawr, PA 19010, USA
[d] Denver Museum of Nature and Science, 2001 Colorado Boulevard, Denver, CO 80205, USA
[e] Department of Earth Sciences, University of California, Riverside, CA 92521, USA
[f] Department of Geology and Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20742, USA
[g] Museo de Paleontología, Departamento de Biología Evolutiva, Facultad de Ciencias, Universidad Nacional Autónoma de México, Ciudad Universitaria, México DF, México

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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, $\delta^{34}S_{CAS}$ variability is consistent with regionally low marine sulfate concentrations during this period. Values of $\Delta^{34}S$ ($\delta^{34}S_{CAS}$–$\delta^{34}S_{pyr}$) 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 ~2 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 $\delta^{34}S_{sulfate}$ among multiple basins was briefly interrupted ~580 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 $\delta^{34}S_{CAS}$ 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; Jensen et al., 1998; Conway Morris, 1998; Knoll and Caroll, 1999; Xiao and Laflamme, 2009). Whereas the triggers for the evolution

* Corresponding author at: Department of Earth and Space Sciences, University of California, Los Angeles, 595 Charles Young Drive East, Los Angeles, CA 90095, USA. Tel.: +1 11 949 338 2461.
E-mail addresses: seanloyd@ess.ucla.edu (S.J. Loyd), pmarenco@brynmawr.edu (P.J. Marenco), Whitey.Hagadorn@dmns.org (J.W. Hagadorn), timothyl@ucr.edu (T.W. Lyons), kaufman@geol.umd.edu (A.J. Kaufman), fst@hp.fciencias.unam.mx (F. Sour-Tovar), fcorsett@usc.edu (F.A. Corsetti).

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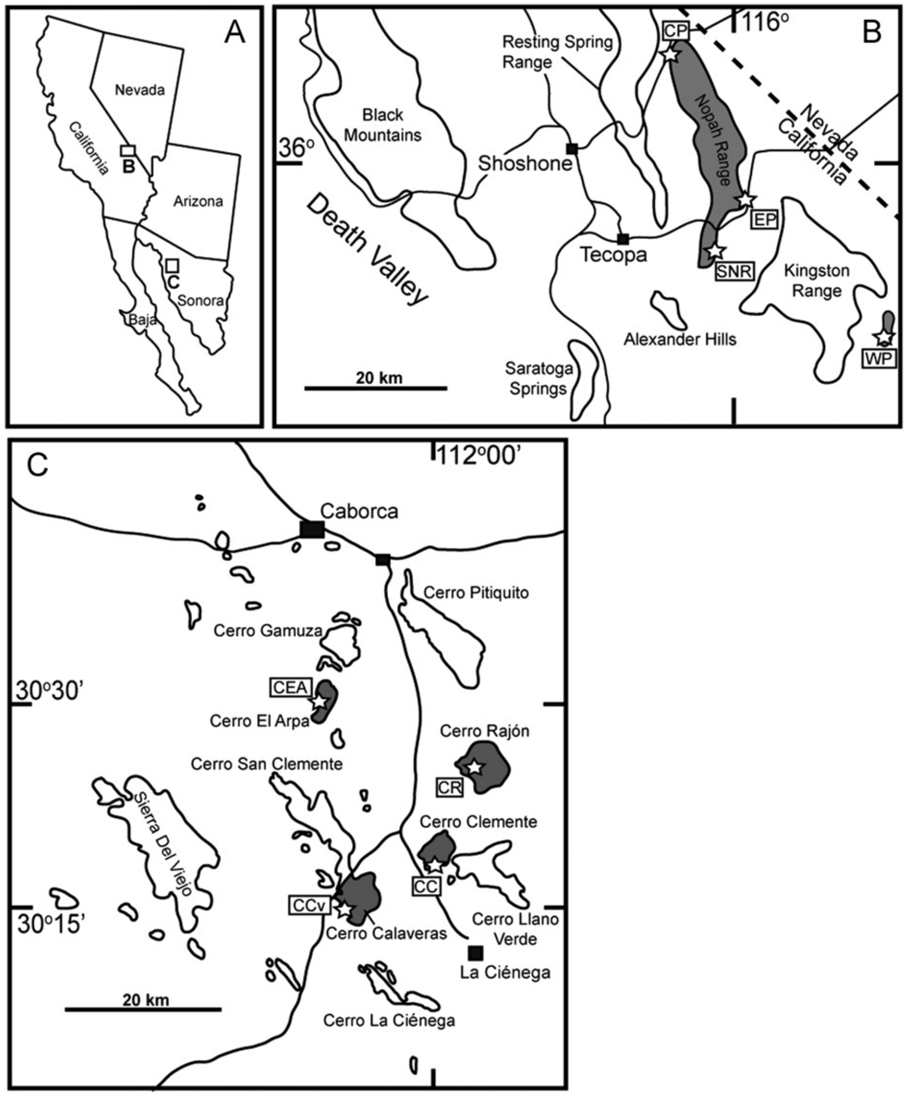

Fig. 1. Regional (A) and local maps of the Death Valley (B) and Sonora (C) Neoproterozoic-Cambrian successions. Shaded regions highlight mountain ranges of sampled outcrops. Stars indicate precise sample sites: CP=Chicago Pass, EP=Emigrant Pass, SNR=Southern Nopah Range, WP=Winters Pass Hills, CR=Cerro Rajón, CEA=Cerro El Arpa, CC=Cerro Clemente, CCv=Cerro Calaveras. Samples of the SNR and WP are from Hurtgen et al. (2004) and Kaufman et al. (2007), respectively.

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.