Chemical Geology 351 (2013) 195–208

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Shallow water redox conditions from the Permian–Triassic boundary microbialite: The rare earth element and iodine geochemistry of carbonates from Turkey and South China

Garrison R. Loope *, Lee R. Kump, Michael A. Arthur

Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, USA

ARTICLE INFO

Article history:
Received 25 September 2012
Received in revised form 4 May 2013
Accepted 15 May 2013
Available online 24 May 2013

Editor: U. Brand

Keywords:
End-Permian extinction
Permian–Triassic boundary microbialite
Ce anomaly
Anoxia
South China
Turkey

ABSTRACT

Redox sensitive elements serve as useful proxies of the oxygenation state of ancient environments, but their interpretation may not always be straightforward. To evaluate the inherent complexities, rare earths and yttrium (REY), iodine, and major element concentrations are determined in two carbonate sections spanning the Permian–Triassic (P–Tr) transition in Demirtas, Turkey and Cili, South China. We use major oxides to identify non-seawater REY sources such as siliciclastics, Fe-oxides, phosphates and diagenetic fluids. Additionally, we employ Y/Ho ratio, La anomaly, and light rare earth element depletion to identify which samples preserve a seawater-like REY_{SN} distribution. In contrast to past interpretations, we find that the P–Tr boundary microbialites in both sections contain REY signatures indicative of deposition in an oxic environment. These boundary microbialites have their base at the extinction horizon and are widespread within the Tethyan region. In the Cili section, the underlying Permian limestone also preserves a seawater-like REY signature with a negative Ce anomaly. This indicates that the water column was oxygenated both before and after the extinction event. The Permian limestone in the Demirtas section does not preserve a seawater-like REY_{SN} distribution, so the absence of a Ce anomaly cannot be used to distinguish prevailing redox conditions during deposition. However, in these samples, we find the presence of a diverse Permian benthic community sufficient to identify deposition in an oxic environment. The geochemical evidence for a continuously oxic environment during the deposition of the boundary microbialite presented in this study strongly supports work done using ostracods as redox indicators within the boundary microbialite in South China. The microbialite has been proposed as a disaster facies, in part resulting from the exclusion of grazers. Although anoxia is one of the suggested mechanisms for the exclusion of grazers, we find that it is not supported by geochemical and biotic evidence.

1. Introduction

The end-Permian mass extinction [~252 Ma] was the most severe biodiversity crisis of the Phanerozoic and is estimated to have caused the extinction of up to 96% of marine species (Raup, 1979). Determining the cause of this extinction has been the focus of much scientific investigation and has led to a wide range of hypotheses for the cause of the extinction (Hallam, 1989; Renne and Basu, 1991; Wignall and Hallam, 1992; Erwin, 1994; Isozaki, 1997; Krull and Retallack, 2000; Kump et al., 2005; Knoll et al., 2007; Brand et al., 2012; Joachimski et al., 2012). Many hypotheses (Wignall and Hallam, 1992; Kump et al., 2005; Meyer et al., 2008; Algeo et al., 2010) incorporate anoxia and euxinia (presence of aqueous hydrogen sulfide) because of the evidence supporting low O_2 and high H_2S in the Late Permian–Early Triassic oceans. The data that support anoxia and euxinia come from many different indicators from a wide geographic range, but there is still much disagreement on the timing and extent of anoxia and euxinia. Sedimentological and geochemical evidence including fine laminations, small pyrite framboids, dysaerobic benthos, high Th/U ratios, and a negative shift in $\delta^{238}U$ suggest a nearly synchronous onset at the extinction event (Wignall and Twitchett, 2002; Wignall et al., 2005; Brennecka et al., 2011). In contrast, other studies have found evidence for anoxia and even biomarkers for photic zone euxinia starting well before the extinction (Isozaki, 1997; Cao et al., 2009; Hays et al., 2012).

Across much of the Tethys, the diverse carbonate reef-deposits of the Late Permian were abruptly replaced by microbialites at the extinction horizon (Kershaw et al., 2011). An invasion of anoxic, CO_2-rich waters onto the carbonate shelves has been proposed as a mechanism that would both stimulate carbonate precipitation by increasing microbial photosynthesis and eliminate the grazers that feed on microbial mats (Lehrmann et al., 2003; Pruss and Bottjer, 2004; Groves et al., 2005).

Despite the interest in anoxia at the mass extinction, only two studies have investigated the paleo-redox conditions of the P–Tr boundary microbialite and these have found conflicting evidence. Liao et al. (2010) reported framboidal pyrite size distributions from

---

* Corresponding author at: 1300 N 37th St. Lincoln, NE 68503, USA. Tel.: +1 814 769 0559.
E-mail addresses: gloope@gmail.com (G.R. Loope), lrk4@psu.edu (L.R. Kump), maa6@psu.edu (M.A. Arthur).

0009-2541/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2013.05.014

the Laolongdong microbialite and concluded that they likely represented the lower-dysoxic environment (Bond and Wignall, 2010). Although the size distribution of these framboids does suggest a low-oxygen environment, framboids of similar size are reported in sediments below fully oxic water bodies (Wilkin et al., 1996). Forel et al. (2009) used ostracod trophic groups to interpret redox condition of the boundary microbialite. They found that the deposit-feeding guild was dominant, which indicates a well-oxygenated environment. An oxic interpretation has also been recently suggested for Early Triassic (Spathian) microbialites in the Moenkopi Formation at Lost Cabin Spring, Nevada on the basis of low organic carbon and pyrite contents (Marenco et al., 2012). Although the Spathian microbialites were deposited after the boundary microbialite, they have also previously been suggested to represent episodic flooding of anoxic, high-alkalinity water onto carbonate shelves (Pruss and Bottjer, 2004; Mata and Bottjer, 2011).

In this study we examine the distribution of rare earths and yttrium (REY) and iodine in two carbonate sections containing boundary the microbialite from Demirtas, Turkey, and Cili County, China (Fig. 1), in order to better constrain the redox conditions of shallow-water environments through the P–Tr transition. We find that a straightforward application of the Ce anomaly redox proxy for all samples leads to an apparent paradox with paleontological data as reported by Kakuwa and Matsumoto (2006). We then use techniques of REY analysis developed on modern and ancient microbialites (Webb and Kamber, 2000; Kamber and Webb, 2001; Van Kranendonk et al., 2003; Nothdurft et al., 2004) to integrate the geochemical redox indicators with paleontological data and provide a more parsimonious redox history. We also test the applicability of a recently proposed redox indicator, iodine, in our sections. By obtaining a better understanding of the redox conditions of shallow carbonate platforms during the Late Permian–Early Triassic, we can evaluate anoxia and euxinia as kill-mechanisms and as drivers of the associated abrupt transition to a microbially dominated carbonate ecosystem.

1.1. Cerium anomaly redox proxy

The Ce anomaly is a widely used redox indicator that makes use of the high redox sensitivity of Ce and its relative depletion in oxic waters (German and Elderfield, 1990 and references therein). Microbial carbonates have been recently identified as an ideal REY archive because they both faithfully record the distribution of REY in the water column and have relatively high overall REY concentrations (Webb and Kamber, 2000). The Ce anomaly has been typically calculated as $Ce/Ce^* = 2[Ce_{SN}]/([La_{SN}] + [Pr_{SN}])$ (Bau and Dulski, 1996) where all concentrations are normalized to a shale composite (indicated as SN; usually PAAS; McClennan, 1995). Unfortunately, interpretation of Ce anomalies is complicated by the anomalous behavior of La in seawater. Although not widely considered until ICP-MS allowed the measurement of Pr, a positive La anomaly is characteristic of seawater (De Baar et al., 1991). To avoid the influence of La while calculating the Ce anomaly, Bau and Dulski (1996) proposed that a negative Ce anomaly be defined by $Pr/Pr^* > 1.0$ where $Pr/Pr^* = 2[Pr_{SN}]/([Ce_{SN}] + [Nd_{SN}])$. We prefer this notation because values of $Pr/Pr^* > 1.0$ only occur in Ce depleted conditions (e.g. oxygenated waters). However, we report both Pr/Pr^* and Ce/Ce^* in this study in order to facilitate comparisons with studies that lack Pr data.

1.2. Iodine redox proxy

Iodine is highly sensitive to changes in redox conditions and has been recently proposed as an indicator of shallow-water redox conditions in carbonates (Lu et al., 2010). The iodine redox proxy remains relatively unproven but may be of great use in shallow carbonate environments because of its potential to record more subtle changes in pO_2 that are expected to occur in shallow-water environments. In this study we test the applicability of the iodine proxy in a period where it is thought that shallow waters became depleted in dissolved oxygen.

2. Geological background

2.1. Cili section

The Cili section is located outside of Kangjiaping in Cili County, northwestern Hunan, China. During the Late Permian and Early Triassic Cili was part of the Jiangan carbonate platform (Wang et al., 2009) that stretched across much of central China in what was the equatorial, eastern Tethys (Fig. 1). The biostratigraphy of the section is described in Wang et al. (2009), while the isotopic geochemistry is published in Luo et al. (2010, 2011). The section spans the Upper Permian Changxing and the Upper Permian-Lower Triassic Daye Formations (Fig. 2), and shows no evidence of a disconformity at the boundary (Wang et al., 2009; Luo et al., 2010).

The Changxing Formation is a matrix supported bioclastic limestone with abundant foraminifera, ostracods and echinoderms. Above this, at

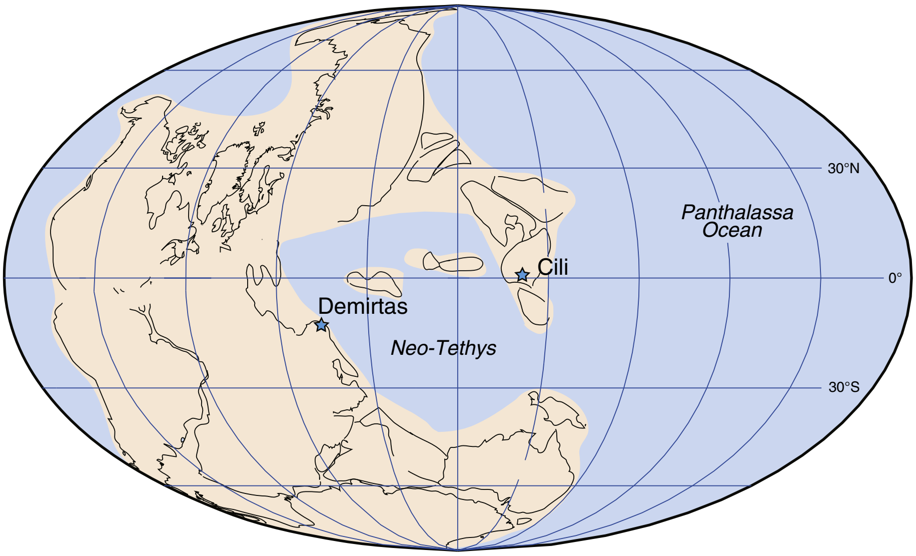

Fig. 1. Paleogeographic map with location of the Cili and Demirtas sites presented in this study (modified from Muttoni et al., 2009).