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Oxygenation in carbonate microbialites and associated facies after the end-Permian mass extinction: Problems and potential solutions



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Abstract Carbonate sediments deposited in normally-oxygenated shallow ocean waters of the latest Permian period, immediately prior to the end-Permian mass extinction, contain well-developed diverse shelly faunas. After the extinction of these skeletal metazoans, the sediments commonly comprise microbialites (regarded by most authors as benthic) and associated facies bearing evidence interpreted by many authors to indicate reduced oxygenation of the shallow ocean waters. However, the evidence of oxygenation state is inconsistent and the sequences have gaps, indicated in the following 5 points:

1) Shelly fossils occur commonly in post-extinction shallow marine limestones, and likely to have been aerated in contact with the atmosphere. Nevertheless, although the largest mass extinction in Earth history may have caused reduced body size in shelly organisms, such reduction is arguably due to environmental stress of lowered oxygenation. Discriminating between these controls remains a challenge.

2) Abundant pyrite framboids in many post-extinction limestones are interpreted by several authors as indicating dysoxic contemporaneous waters, so the organisms that lived there, now shelly fossils, were dysaerobic. However, verification is problematic because pyrite framboids scattered amongst shelly fossils cannot have formed amongst living organisms, which need at least some oxygen; synsedimentary framboid formation requires anoxic conditions in the redox boundary where sulphate-reducing processes work. Thus, framboids and shelly fossils found together means taphonomic mixing of sediments, destroying original depositional relationships so that it is not possible to determine whether the shells were aerobic or dysaerobic prior to sediment mixing. Furthermore, diagenetic growth of framboids is possible, as is import of previously-formed framboids from deeper water during upwelling. Thus, there is no proof of an environmental link between framboid size and occurrence, and contemporaneous oxygenation in these post-extinction shallow water facies, so we question the validity of this model in those facies, but consider that the model is valid for deeper water facies.

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3) Some publications provide evidence of oxygenation, from redox-sensitive elements in post-extinction limestones, while others indicate low oxygen conditions. Redox-sensitive geochemistry requires further work to explore this issue at higher resolution of sampling than has been so far applied.

4) Biomarkers recorded in some post-extinction facies contain evidence of anoxic conditions (including green sulphur bacteria) but other examples lack these, which may be indicate fluctuations of water oxygenation. However, a key issue that has not yet been resolved is determination of whether biomarkers were imported into the sites of deposition, for example by upwelling currents, or formed where they are found. Thus, there is currently no verification that biomarkers of low oxygen organisms in shallow water settings actually formed in the places where they are sampled.

5) The common occurrence of small erosion surfaces and stylolites represents loss of evidence, and must be accounted for in future studies.

The oxygenation state of post-end-Permian extinction shallow marine facies continues to present a challenge of interpretation, and requires high-resolution sampling and careful attention to small-scale changes, as well as loss of rock through pressure solution, as the next step to resolve the issue.

Keywords Stromatolite, Thrombolite, Microbialite, Permian–Triassic boundary, Pyrite, Anoxia

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1. Introduction and aims

The state of ocean oxygenation through the end-Permian extinction event is a topic of intense scrutiny in numerous publications and a range of evidence exists using: (a) sedimentary facies and fossils (e.g., Algeo et al., 2011, 2013; Baud et al., 2007; Farabegoli et al., 2007; Forel et al., 2009; Kershaw et al., 2007; Twitchett and Wignall, 1996; Xie et al., 2010); (b) biomarkers (e.g., Grice et al., 2005a; Luo et al., 2013; Nabbefeld et al., 2010a; Xie et al., 2005, 2007; Zhou et al., 2017); (c) physical proxy of pyrite framboids (e.g., Bond and Wignall, 2010; He et al., 2013; Liao et al., 2010, 2017; Tian et al., 2014); and (d) geochemical proxies of oxygenation (e.g., Algeo et al., 2007, 2008; Collin et al., 2015; Lau et al., 2016; Meyer et al., 2008; Nabbefeld et al., 2010b; Ryskin, 2003; Song et al., 2014). Although there is good evidence for reduced oxygen conditions in the deeper ocean system (e.g., Bond and Wignall, 2010; Lau et al., 2016; Wignall and Newton, 1998), even in shelf settings (e.g., Fenton et al., 2007; Tian et al., 2014), there is continuing debate about the degree to which shallow shelf waters were oxygenated, important because these are environments of many post-mass-extinction facies including carbonate microbialites that have become symbolic of post-end-Permian extinction environments. This paper focuses on carbonate microbialites that formed after the extinction of skeletal metazoans (therefore considered in this paper as postextinction microbialites) and their associated facies,

because they are very common in shallow marine facies across the end-Permian extinction; however, shallow marine clastic sequences in northern Pangaea (*e.g.*, Wignall *et al.*, 2016) containing evidence of anoxia indicate the widespread nature of the oxygenation issue.

Because most localities show microbialites cross the Permian-Triassic boundary as defined by the first appearance of the Hindeodus parvus conodont (e.g., Jiang et al., 2007), we refer to them as Permian-Triassic boundary microbialites (PTBMs, see also Kershaw et al., 2007, 2012a). Before extinction there are: high diversity biotas (e.g., Chen and Benton, 2012), rare pyrite framboids (popular indicators of contemporaneous environmental oxygen levels, see Bond and Wignall, 2010, demonstrating rare framboids in some sections before the extinction), and limited evidence of the types of biomarkers indicative of low environmental oxygen (e.g., Luo et al., 2013) show aerobic biomarkers, while Nabbefeld et al., 2010a show fluctuations that indicated changes in oxygenation). After extinction of most skeletal metazoans there are: low diversity biotas (e.g., Erwin, 2006), and abundant widespread microbialites (e.g., Baud et al., 2007), abundant pyrite framboids in most PTB sites (e.g., Bond and Wignall, 2010); some evidence of biomarkers for extreme anoxic conditions of photic zone euxinia (Grice et al., 2005b; Luo et al., 2013; Nabbefeld et al., 2010a); and redox-sensitive geochemical indicators that the environments for the PTBMs were normally oxygenated (e.g., Collin et al., 2009). Lei et al. (2017) interpreted fluctuating

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