Assessing the Reliability of Early Marine Cements in Recording Changes in Seawater Redox Conditions Across the Late-Devonian Mass Extinction

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Abstract

The Late-Devonian Mass Extinction (LDME) extinguished up to 40% of all marine species, with evidence suggesting marine anoxia was the primary cause. This study performs rare earth element analysis of early marine cements from reefal limestones from Australia and Scotland to show that these cements capture a marine anoxic signature across the LDME for the first time, directly implicating marine anoxia and by extension, the rise of land plants, as the cause of the LDME. This work also demonstrates that early marine cements serve as reliable proxies for recording changes in seawater redox conditions over whole-rock analysis.

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Introduction and Motivation

The Late-Devonian Mass Extinction (LDME) is one of the "big 5" mass extinctions (Raup *et al.* 1982) and occurred approximately 371.9 million years ago (Ma) (Racki 2021). The extinction event lasted roughly 1 million years (Myr) and, uniquely, was characterised by up to 5 "bursts" of species death, each of varying severity (McGhee *et al.* 2021). The LDME preferentially targeted shallow-water marine species, particularly coral reef ecosystems which, prior to the extinction, covered up to 5 million square kilometres of the global oceans – roughly 10 times the surface area covered by modern reef ecosystems (Martin-Garin *et al.* 2023). Following the LDME, reef areal extent reduced by a factor of up to 5000 (McGhee *et al.* 2021). A number of reef-building species, including tabulate and rugose corals, and stromatoporoid sponges, failed to re-proliferate to pre-extinction levels (Wood 2004) and disappeared from the geological record for up to 30 Myr (Yao *et al.* 2015). Cumulatively, current estimates suggest that up to 40% of marine species went extinct by the end of the LDME (Stanley 2016).

In contrast to the mass species death within the global oceans, on land, life was flourishing. The Devonian period is now well-known as the time at which land plants first colonised the majority of Earth's land-surface, culminating in the colonisation of dry, upland continental interiors by vascular land plants, and the first developments of forest ecosystems (arborescence) (Kabanov *et al.* 2023). It is this Devonian rise of land plants that is thought to have driven one of the greatest oxygenation events in earth history (Wallace *et al.* 2017); indeed, by the early Carboniferous, atmospheric oxygen (pO_2) levels reached 21% from 10-12% in the early-Devonian, matching present-day levels (Dahl *et al.* 2010). Such connections between the rise of land plants and atmospheric oxygenation, as well as a number of global environmental changes, ultimately led Algeo *et al.* 1995 to suggest that the rise of land plants was responsible for causing the LDME when they proposed the land-plant weathering hypothesis. This hypothesis suggests that the development of arborescence and an increase in the abundance of deeply-rooting plants would increase global rates of continental chemical weathering and drive the deposition of greater volumes of nutrients (chiefly nitrogen and phosphorus) to the oceans via river systems (Algeo *et al.* 1998). Such increases in nutrient supply would enhance shallow-marine productivity, stimulating algal blooms and driving

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widespread surface eutrophication and, ultimately, marine anoxia, proving fatal to many marine species (Algeo *et al.* 1995).

Marine anoxia is commonly expressed in the geological record through the presence of bituminous black-shale horizons that represent an accumulation of large quantities of organic matter, preserved under anoxic surface waters (Poty *et al.* 2011; Yao *et al.* 2015). Whilst such black-shale horizons are globally ubiquitous, and have been dated to coincide with the events of the LDME (Buggisch 1972), not all shallow-marine environments are prone to developing conditions which facilitate black-shale deposition. As such, it is necessary to turn to the geochemical proxy record to assess redox conditions at this time. To do this, early marine cements, formed within reefal limestones upon early formation of the limestone itself, which have not previously been used to understand the changing seawater redox changes across the LDME, have been investigated here to deduce whether or not marine anoxia is recorded by these cements, and to assess their ability to record reliable geochemical signatures.

Methods

In order to analyse the long-term seawater chemistry changes that may have occurred across the LDME, samples of pre-extinction (Frasnian), mid-extinction (Famennian), and post-extinction (Carboniferous) -age reefal limestones were analysed from the Canning Basin in Western Australia (Frasnian and Famennian), and from Roscobie Quarry in Fife, Scotland (Carboniferous), respectively. Early marine cements within these samples have been targeted by this study where previous studies have suggested that they are reliable proxies for recording seawater chemistry because they directly precipitate from the seawater in which they form (Webb *et al.* 2000; Nothdurft *et al.* 2004; Wallace *et al.* 2017; Xiong *et al.* 2023). The rare earth element (REE) cerium (Ce), present in trace amounts within these early marine cements, was analysed to measure the oxidation state of the seawater within which the cements formed. Where other REE's, such as lanthanum (La) and neodymium (Nd) exist in trivalent oxidative states, trivalent Ce is instead converted to an insoluble tetravalent state in well-oxygenated seawater (German *et al.* 1990), and so can be used as a measure of oxidative Ce removal (Xiong *et al.* 2023) when compared to the abundance of trivalent Ce to other trivalent REE's. This relative abundance, represented through a 'cerium anomaly' (Ce_{anom}), can indicate whether the cements formed in oxygenated or anoxic seawater (Banner *et al.* 1988; Tostevin *et al.* 2016) and, as such, can inform us about the redox state of the seawater within which they precipitated. Should a Ce_{anom} be negative ($Ce_{anom} < 1$, indicating conversion of trivalent Ce to tetravalent Ce), then the early marine cements precipitated in oxygenated seawater, and where a Ce_{anom} is positive ($Ce_{anom} > 1$, indicating little to no conversion of trivalent Ce to tetravalent Ce), then the early marine cements precipitated in poorly-oxygenated or anoxic waters (Xiong *et al.* 2023).

The Ce_{anom} of early marine cements from this study are plotted through time to understand the longer-term oxygenation status of seawater before, during, and after the LDME (Figure 1) and were compared against other studies which derived their Ce_{anom} data from whole-rock data as opposed to directly targeting early marine cements.

Results

Results from this study indicate that immediately prior to the LDME, early marine cements were forming within seawater that was weakly oxygenated, with occasional interactions with at least dysoxic waters, where Frasnian Ce_{anom} values range between 0.972 and 1.121. However, during the LDME, seawater redox conditions were highly dynamic, fluctuating between strongly oxygenated and strongly anoxic waters, with Famennian Ce_{anom} values ranging between 0.203 to 1.400. Results from this study suggest that seawaters were well-oxygenated post-extinction, with Carboniferous Ce_{anom} values ranging between 0.745 and 0.831.

The Ce_{anom} values captured in this study record the onset of anoxic conditions that continued into the LDME, which suggests marine anoxia was the primary driver of the LDME (Wallace *et al.* 2017). The fact Ce_{anom} values continue to record highly oxygenated seawaters in the Famennian suggests that the rise of land plants was responsible for driving the LDME, where the development of arborescence in the mid-Devonian drove an increase in pO_2 to levels comparable to modern-day levels by the Famennian (LDME). Famennian Ce_{anom} values also suggest that arborescence caused increased continental weathering and the transport of elevated concentrations of nutrients to the global oceans sufficient to cause shallow-marine

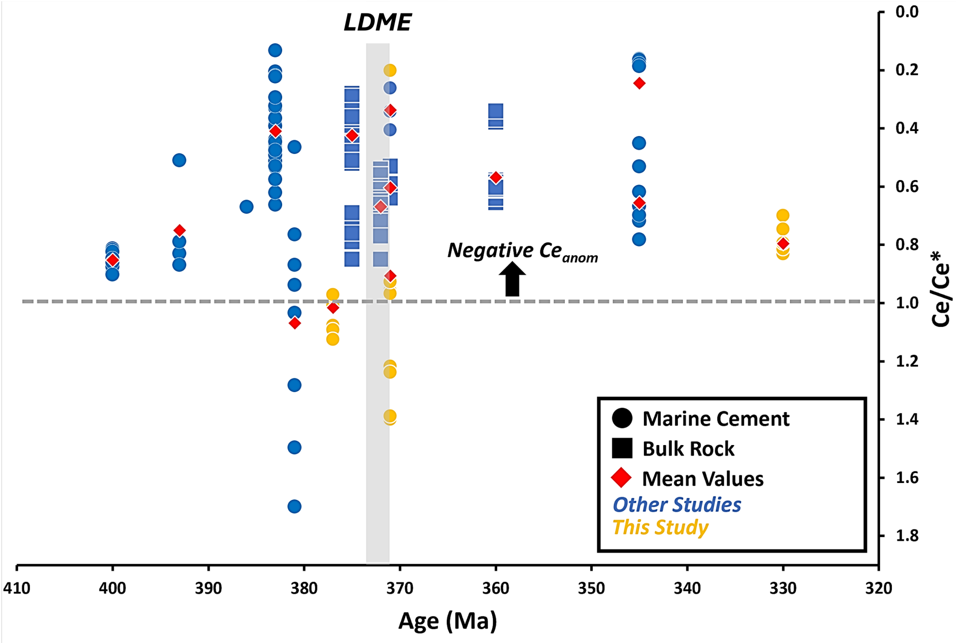

Figure 1: Plot of compiled Ce anomaly data from this study and from other studies (Nothdurft *et al.* 2004; Ma *et al.* 2008; Zeng *et al.* 2011; Franchi *et al.* 2016; Wallace *et al.* 2017; Kalvoda *et al.* 2018) displaying values for data derived from early marine cements and whole (bulk) rock data from carbonate rocks. Ce/Ce* denotes the cerium anomaly. Note that the grey shaded area marks the approximate timing of the LDME. Blue data points represent data gathered from other studies, whereas yellow data points represent data gathered from this study. Square data points indicate whole-rock data, whereas circle data points indicate early marine cement data. Mean values for each data-set included in the plot are represented by red diamonds.

eutrophication and mass species death (Algeo *et al.* 1995; Edwards *et al.* 2015; Wallace *et al.* 2017) as evidenced by occasional incursions of strongly anoxic seawater during the Famennian.

It should be noted that, of the studies included in Figure 1, only those studies which used early marine cements (see Ma *et al.* 2008; Wallace *et al.* 2017) were able to capture marine anoxia across the LDME. Studies which analysed whole-rock samples, without isolating early marine cements, failed to capture the true dynamic nature of seawater redox through the LDME, suggesting that greater emphasis should be placed on utilising early marine cements to analyse changing seawater chemistry.

Conclusion

This study demonstrates that the rise of land plants can likely be implicated in causing the LDME, where cerium anomalies within reefal limestone early marine cements record incursions of anoxia throughout the time of the mass extinction interval. cerium anomalies also record periods of seawater oxygenation, particularly into the lower Carboniferous, where early marine cements record only negative Ce_{anom}. Such Ce_{anom} values in the Carboniferous reflect the stabilisation of seawater redox conditions following the development of arborescence, as well as the colonisation of continental interiors, to more oxygenated conditions, following initially high nutrient inputs as a result of greatly enhanced continental weathering during the initial stages of the development of forest ecosystems, which is itself represented in the positive Ce_{anom} values seen during both the Frasnian and Famennian periods coincident with the LDME.

Further work is needed to place the Ce_{anom} results from this study into a more robust framework in order to determine whether specific instances of marine anoxia can be dated to coincide with the five bursts of species death which characterise the LDME.

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