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Zunli Lu , Wanyi Lu , Rosalind E. M. Rickaby , Ellen Thomas
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1 Introduction

The history of oxygen, as both a planetary biosignature of and a requisite for all complex life, has been the focus of a growing research community for decades (e.g., Holland, 2006). To understand and trace how the surface of Earth evolved from largely anoxic to an oxygenated system of rich ecological diversity, numerous proxies have been proposed, developed, and cross-examined thoroughly in a wide variety of geologic records (e.g., Lyons et al., 2014). More and more nuances in Earth's oxygen history are being revealed, revising earlier conceptual models into reconstructions of oxygen levels in four dimensions (3-D space and time) at ever increasing spatial and temporal resolution. Rather than the "classical" model of a two-step rise in oxygen to modern levels in Earth's atmosphere and oceans, additional oxygenation events have been proposed for the generally low-oxygen world of Proterozoic and even early Paleozoic times (e.g., Dahl et al., 2010; Diamond et al., 2018). In addition, an increasing number of oxygen depletion events have been suggested as punctuating the high-oxygen world of the Phanerozoic Eon (e.g., Jenkyns, 2010). There is an emerging need to better constrain and calibrate proxies for individual components of the Earth system (e.g., atmosphere, surface ocean, deep ocean), and for individual redox windows (e.g., oxic–hypoxic, hypoxic–anoxic, anoxic–euxinic). Regardless of the wave of paleo-redox proxy development sweeping across the periodic table, there are, clearly, open niches for proxies based on carbonate records, proxies specifically targeting relatively shallow and surficial parts of the water column, and proxies for the oxic–suboxic redox window. For such applications, the carbonate iodine-to-calcium ratio (I/Ca) has been developed as the iodine proxy for oxygen (iprOxy).

2 Proxy Systematics

Iodine is a redox-sensitive biophilic element. Its fluxes in/out of seawater are small relative to the amount of iodine recycled within the water column through biological production and remineralization (Lu et al., 2010). Iodine has a long residence time of ~300 kyr (Broecker and Peng, 1982), and it has a biointermediate element distribution rather than a nutrient-like or scavenging distribution (Farrenkopf et al., 1997b). The redox chemistry of iodine in the atmosphere and seawater may involve many different iodine species. However, the iodine species most relevant to the I/Ca proxy are iodide (I^-) and iodate (IO_3^-), which are thermodynamically most stable in anoxic and oxic seawaters, respectively. A number of studies have been dedicated to the redox chemistry of iodine in seawater (Amachi et al., 2007; Cutter et al., 2018; Farrenkopf et al., 1997a; Farrenkopf and Luther, 2002; Luther and Campbell, 1991; Luther et al., 1995; Rue et al., 1997; Wong and Brewer, 1977; Wong and Cheng, 2008; Wong and Zhang, 2003; Wong et al., 1985). The reduction of iodate to iodide is generally fast, leading to the predominant presence of iodide in low-oxygen water, with very limited exceptions (e.g., Cutter et al., 2018; Rue et al., 1997). The oxidation of iodide to iodate can be kinetically slow (e.g., Hardisty et al., 2020), which may cause low concentrations of iodide to persist in oxygenated waters (e.g., Chance et al., 2014).

Laboratory crystal synthesis experiments (Lu et al., 2010; Zhou et al., 2014), synchrotron studies (Kerisit et al., 2018; Podder et al., 2017), and modeling (Feng and Redfern, 2018) show that iodate is incorporated in the calcite structure by substituting for the carbonate ion with charge compensation through Ca^{2+} substitution (e.g., Na^{+}), whereas iodide may be excluded from the mineral lattice. Hence, I/Ca values of carbonate should record changes in iodate concentrations in the water. If the dissolved oxygen level is the dominant control on the iodate concentration, then I/Ca can, to a first-order approximation, be used as a proxy for dissolved oxygen.

The advantages of I/Ca in calcite as a proxy are several-fold. It is a relatively simple, fast, and cost-effective analysis on the inductively coupled plasma-mass spectrometry (ICP-MS), allowing the possibility to construct records at high temporal resolution. Small volumes of sample materials are required for analyses, allowing measurements on micro-drilled samples and microfossils such as foraminifera (<0.5 mg). I/Ca should record local redox conditions, and therefore can be used as a complementary tool and combined with other proxies reflecting global changes. Multiple I/Ca records for the same time interval from different locations and water depths (e.g., Lu et al., 2020; Zhou et al., 2015) can provide a unique opportunity to reconstruct ocean oxygenation truly in four dimensions (3D space and time). Since the conversion between iodide and iodate is very sensitive to low levels of dissolved oxygen (instead of euxinia, with H_2S present), I/Ca signals are expected to track hypoxia or suboxia, which cannot be reconstructed by most redox proxies commonly used in Earth System Science.

However, it is important to note the main limitations of I/Ca. I/Ca is certainly not immune to post-depositional alteration (Hardisty et al., 2017), just as any other carbonate-based proxy. With a rising interest in measuring I/Ca in different laboratories, it is important to maintain consistency in analytical methods. Owing to the local nature of the I/Ca signal, sampling density may impact the statistical distribution of values. The potentially slow kinetics of iodide reoxidation imply that low iodate –high O_2 waters may exist, highlighting the possibility of I/Ca signals influenced by both oxygenation and water mass mixing. Based on all the foregoing, a major pitfall in the use of I/Ca is applying this proxy prematurely for quantitative interpretation of past oxygen levels.

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3 Methods

Iodine concentrations in carbonate were first measured through pyrohydrolysis followed by ICP-MS measurement of the trap solutions (Muramatsu and Wedepohl, 1998). That method was modified to measure I/Ca in carbonate rocks (Lu et al., 2010). In preparation, rock samples are crushed (or drilled) and homogenized to a fine powder. Then ~4 mg of powdered sample is weighed and thoroughly rinsed with 18 MΩ water to remove soluble iodine (adsorbed or residual salt). Diluted nitric acid (3%) is added to dissolve carbonate. The solutions are diluted to a consistent matrix with ~50 ppm Ca, and 5 ppb indium and cesium are used as internal standards. The final solutions contain 0.5% tertiary amine to stabilize iodine in solution and ensure a reasonably short rinse time on the ICP-MS. The measurements immediately follow solution preparation to minimize changes in iodine speciation or volatilization. Fresh calibration standards are made from KIO_3 powders daily, for each batch of measurements. In the past, nitric acid was added to the final solutions loaded into the nebulizer to make them mildly acidic, and iodine was measured with a range of trace elements such as Mn, Sr, and rare earth elements (Lu et al., 2010). However, this methodology has evolved to use of an alkaline matrix and measurement of iodine with Ca and Mg only, to better avoid iodine speciation change due to the addition of acids, while all other trace elements are measured in separate runs in acidic solutions (e.g., Lu et al., 2016).

I/Ca measurements can be performed on a sensitive quadrupole ICP-MS (e.g., Varian/Bruker models) or magnetic sector ICP-MS (Thermo Element Series). The sensitivity of I-127 is typically tuned to 80,000–100,000 counts per second for a 1 ppb standard at Syracuse University and formerly at the University of Oxford. It is important to report the sensitivity of the 1 ppb I-127 standard on different instruments, especially when attempting to resolve I/Ca signals of 0–1 μmol/mol or even 0–0.5 μmol/mol. Instruments with lower sensitivity can produce useful data in some cases, such as large stratigraphic variations in I/Ca. The reliability of I/Ca data in a particular study should not be judged solely by the instrument sensitivity, but should be evaluated in the broader context, including stratigraphic settings and multiproxy comparison. However, the instrumental sensitivity on I-127 should be reported as metadata, so that the community can gradually develop a sense for which instruments are suitable for which types of I/Ca applications. Furthermore, I-127 concentrations in the solutions fed into the ICP-MS should be monitored over time. For example, groundwater and marine porewater may contain high levels of iodine and raise instrumental background, making it difficult for carbonate I/Ca measurements.

JCp-1 (coral, aragonite) is a calcium carbonate reference material with a published iodine concentration (Chai and Muramatsu, 2007), suitable for

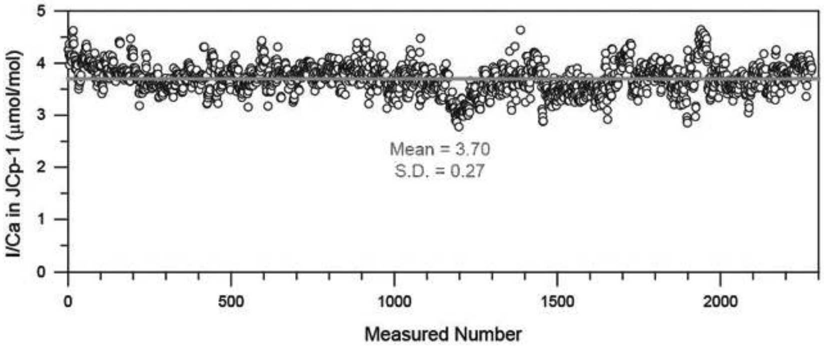

Figure 1 I/Ca values measured in reference material JCp-1 at Syracuse University laboratory in 2011–2018 (*n* = 2,280).

quality control and interlaboratory comparison. Earlier measurements of JCp-1 resulted in I/Ca values of 4.33 ± 0.36 µmol/mol (*n* = 5) (Gakushuin University, Japan) (Chai and Muramatsu, 2007) and 4.27 ± 0.06 µmol/mol (*n* = 8) (University of Oxford, UK) (Lu et al., 2010). More recent work reported lower values of 3.82 ± 0.39 µmol/mol (*n* = 60) (GEOMAR, Kiel, Germany) (Glock et al., 2014), with similar values reported in Hardisty et al. (2017) (UC Riverside, USA). The long-term (2012–2018) records of JCp-1 at the Syracuse University laboratory yielded an average I/Ca value of 3.70 ± 0.27 (1 standard deviation) µmol/mol (*n* = 2,280) (Fig. 1). A JCp-1 measurement is now run between every three to six unknown samples at the Syracuse laboratory. To ensure long-term consistency, the I/Ca values of unknown samples are corrected by adjusting the value of the adjacent JCp-1 measurements to 4.27.

Unfortunately, JCp-1 has been banned from export from Japan in recent years, so an in-house standard (synthetic calcite) has been produced and calibrated to JCp-1. The protocol of preparing synthetic calcite was described in the supplementary materials in Lu et al. (2010). Existing batches of synthetic calcite showed I/Ca values of 3.52 ± 0.27 µmol/mol (n = 248) after corrections with the JCp-1 value measured immediately before the in-house standard. After the I/Ca value has become consistently reproducible in different batches of this in-house standard over a few years, it will be made available to other laboratories on request.

Foraminiferal tests are commonly used in paleoceanographic applications, including isotope and trace element analyses. The cleaning procedure for monospecific foraminiferal tests for I/Ca analyses are modified after Barker et al. (2003) and Lu et al. (2010) and include the removal of clays by rinsing ultrasonically with deionized water, and removal of organic matter by oxidative cleaning with NaOH–H_2O_2 solutions (Glock et al., 2014; Hoogakker et al.,

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2018; Lu et al., 2016). In addition to typical ICP-MS measurements, foraminiferal I/Ca measurements on individual specimens have been attempted with secondary ion mass spectrometry (SIMS) (Glock et al., 2016). High-resolution SIMS-derived I/Ca values within individual specimens (inter- and intratest) may provide information on short-term oxygen variability, whereas bulk ICP-MS analyses on whole specimens may be more suitable for relatively longer term oxygen reconstructions (Glock et al., 2016).

4 Sample Materials and Post-depositional Alterations

Criteria for selecting marine carbonate materials for I/Ca analysis depend on the specific application or research question. For early (e.g., Precambrian) Earth studies, relatively well-preserved dolomites or limestones are suitable for bulk carbonate I/Ca measurements. For samples of younger ages, bivalve shells should be avoided when measuring bulk carbonate I/Ca, since they seem to exclude iodine completely during calcification. Corals and foraminifera generally contain measurable iodine.

A large set of Neogene–Quaternary bulk carbonates (rather than specific fossils) with a varying degree of preservation was used to study the impact of diagenetic processes on the I/Ca signal (Hardisty et al., 2017). Carbonate recrystallization during subaerial exposure to meteoric waters, marine burial in anoxic pore waters, and dolomitization are most likely to reduce carbonate-associated iodine concentrations, likely reflecting the tendency of iodate to be reduced in pore waters. No post-depositional processes tested so far increase the I/Ca in carbonates. Thus, carbonate I/Ca values of ancient rocks provide minimum estimates of local seawater iodate levels (Hardisty et al., 2017). I/Ca analysis can be paired with typical diagenetic screening, such as Mg, Mn, δ^{13} C, δ^{18}O, and cathodoluminescence (e.g., Edwards et al., 2018; Lu et al., 2017; Wei et al., 2019; Wörndle et al., 2019). It is unlikely that any diagenetic proxy will be able to quantitatively and reliably resolve the primary signal of I/Ca. Like any other paleo-environmental proxy, I/Ca should be interpreted carefully, with multiproxy comparison and data-model comparison, and evaluation of the status of carbonate preservation.

5 Long-Term I/Ca Trends Through Earth History

5.1 I/Ca Excursions and pO_2 Rise

I/Ca has been applied at different timescales throughout Earth history, with the long-term record showing both excursions and step changes. I/Ca peaks were recorded in marine carbonates at almost all previously documented major instances of atmospheric O_2 rise, whether well-established or debated (Fig. 2).

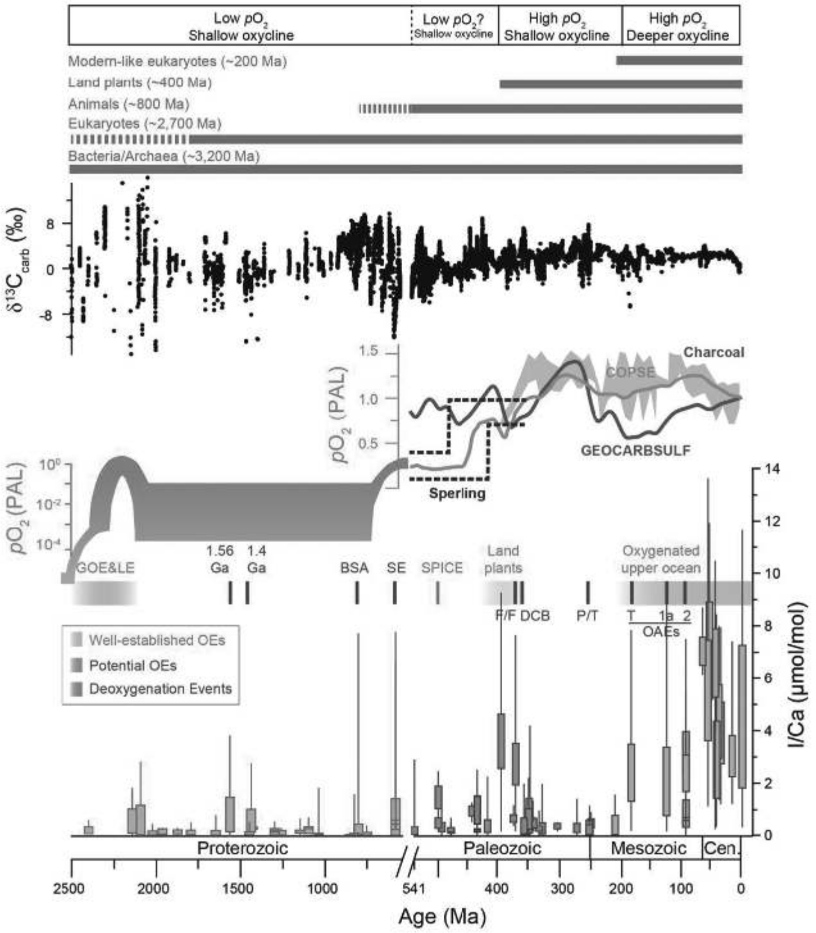

Figure 2 Summary of the long-term carbonate I/Ca record, modified from Lu et al. (2018), and updated with sections from Lowery et al. (2018), Shang et al. (2019), Wei et al. (2019), and Young et al. (2019). The eukaryotic evolution is modified from Knoll (2014). The $\delta^{13}C$ record is from Saltzman and Thomas (2012). The “modern-like eukaryotes” include both “calcifying eukaryote marine plankton” and “the modern evolutionary fauna” in marine vertebrates and invertebrates in the sense of Sepkoski (1981).

No I/Ca signal was detected in the Archean, whereas I/Ca signals can be measured for times during and after the Great Oxidation Event (GOE) at ~2.4 Ga (Hardisty et al., 2014).

Measurement of I/Ca across the GOE is a straightforward application of this proxy to detect the presence of dissolved oxygen during the first rise of O_2 in the atmosphere. The Lomagundi Event at ~2.1 Ga, sometimes considered to be part of the GOE, was suggested to be an "overshoot" of pO_2 (Bekker and Holland, 2012). The I/Ca values then declined in post-GOE Paleoproterozoic and Mesoproterozoic carbonates (~2–1 Ga), with notable exceptions at ~1.4 Ga (Hardisty et al., 2017) and ~1.56 Ga (Shang et al., 2019). Emerging evidence is building for a transient oxygenation event at ~1.4 Ga, for example, from molybdenum isotopes (Diamond et al., 2018) and uranium isotopes (Yang et al., 2017). Several I/Ca peaks in the Neoproterozoic and early Paleozoic (~800–400 Ma) provide evidence for oxygenation events, generally supported by independent geochemical proxies: the Bitter Springs carbon isotope anomaly at ~ 800 Ma (Isson et al., 2018; Wei et al., 2018b), the Ediacaran Shuram carbon isotope excursion at ~ 580 Ma (Sahoo et al., 2016; Shi et al., 2018; Tostevin et al., 2019; Wei et al., 2018a), and the rise of land plants at ~400 Ma (Dahl et al., 2010; He et al., 2019; Wallace et al., 2017).

Relatively high oxygen regions in the early oceans might have been present in a patchy oasis-like fashion (Olson et al., 2013). In addition, a post-depositional decrease in signals would make high I/Ca values harder to find in ancient carbonates. Thus, when maximum values above a low background are used to argue for an oxygenation event, there commonly is the potential caveat associated with sampling density in time and space in these relatively deep time studies, and it is not surprising that higher maximum I/Ca values appear to be found when more sections and more samples per section are measured (Fig. 3).

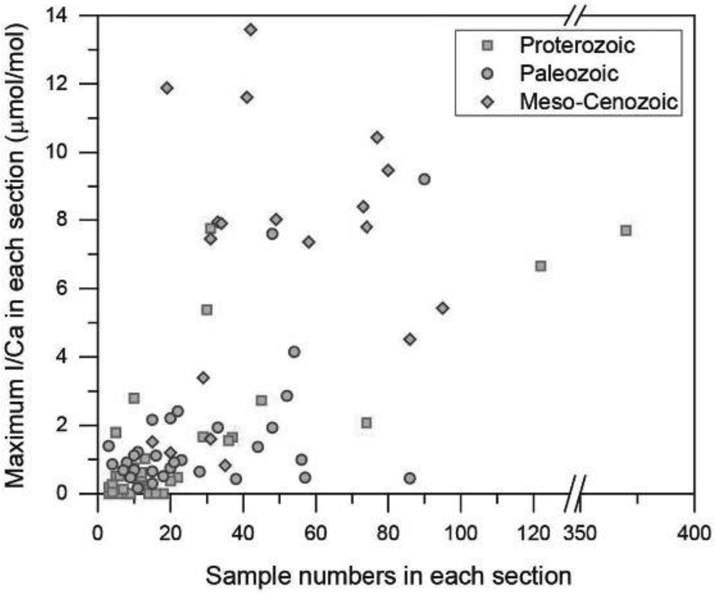

Figure 3 Sampling density vs. maximum I/Ca in each section (data shown in Fig. 2).

However, such cross-plots may exaggerate the sampling bias, particularly in Proterozoic studies. It is a common practice to measure more samples on parts of sections showing high values during preliminary studies (or across a well-known "event"), to obtain better stratigraphic constraints, when the target is high I/Ca values as an indicator of higher oxygen levels. To evaluate whether the maximum I/Ca values differentiating two time intervals were influenced by sampling density, total numbers of sections for each time interval should be compared, as well as total numbers of samples and time resolution.

5.2 Step Changes in I/Ca Baseline

In addition to the high values commonly associated with a global pO_2 increase, background I/Ca values show significant stepwise increases, first across the GOE and then in the Mesozoic (Fig. 2). Increasing diagenetic alteration with increasing age is predicted to cause gradual decreases in I/Ca, and changes in lithology (e.g., dolostone–limestone) do not correlate with the step changes observed here (Hardisty et al., 2017; Lu et al., 2018). Carbonate rocks selected for paleo-environmental reconstructions were precipitated primarily from/in the upper water column; thus the bulk carbonate I/Ca signal is largely controlled by the local upper ocean iodate gradient. I/Ca values are not expected to always correlate with redox proxies responding oxygenated seafloor globally.

Atmospheric pO_2 controls the upper boundary of the vertical iodate gradient, whereas subsurface O_2 consumption in the upper water column (e.g., oxygen minimum zone [OMZ] or oxycline) controls its lower boundary. The two step-changes in the I/Ca record (Fig. 2) likely mark fundamental changes in these boundary conditions. In the pre-GOE scenario, the whole ocean was dominated by iodide in anoxic waters. After the GOE, in contrast, the shallow ocean became oxygenated through mixing with the atmosphere, and at this time the iodate concentration decreased from the sea surface toward the deeper boundary with anoxic waters. Hence the step change across the GOE was related to the pO_2 rise, increasing the iodate concentration at the upper boundary of the iodate gradient. In contrast, the step change in I/Ca in the early Mesozoic was more likely to have been caused by changes in the lower boundary of the iodate gradient, that is, related to an increasing oxycline depth. Similarly low I/Ca baselines in the Neoproterozoic and Paleozoic did not follow the second atmospheric pO_2 rise after the GOE but instead were dominated by the oceanic oxygen signal (shallow oxycline in the water column). This is not surprising, since I/Ca is mainly an oceanic oxygen proxy, though also sensitive to major changes in atmospheric oxygen. Iodate concentrations are typically low above marine OMZs even under modern high atmospheric oxygen condition, implying that high pO_2 should not be automatically assumed to produce high I/Ca baseline in long-term geologic records.

Oxycline depth is controlled by temperature-dependent solubility, ocean ventilation, and organic matter remineralization (Keeling et al., 2009). In the modern ocean, the surface water IO_3^- concentration can be low locally, during shallow hypoxic events (Truesdale and Bailey, 2000). Thus, high I/Ca measured in upper ocean carbonates requires both high pO_2 and a deep oxycline. Among the three factors (temperature-dependent solubility, ocean ventilation, and organic matter remineralization), the only one likely to behave in a stepwise manner on long timescales is the remineralization of organic matter, driven by biological evolution as well as environmental conditions. The influence of remineralization depth on oxycline and OMZ positions was modeled (Meyer et al., 2016). There was no proxy record demonstrating the timing of OMZ changes in the Phanerozoic, whereas the timing for proliferation of calcifying plankton is relatively well known (Fig. 2). The Phanerozoic I/Ca record tentatively points to the early Mesozoic for oxycline changes, consistent in timing with the diversification of calcifying plankton, although more work is needed to constrain the exact timing and rate of change (Lu et al., 2018).

6 Short-Term Ocean Deoxygenation Events

6.1 Paleozoic Extinctions

The Cambrian–Ordovician interval is known for several trilobite extinction events that have been linked to ocean anoxia (Saltzman et al., 2015). Two out of three sections in the Great Basin region, western United States, recorded lower I/Ca values coincident with a 30% extinction of standing generic diversity (Edwards et al., 2018). Coeval δ^{13} C and δ^{34}S excursions have been used to argue for increased global carbon burial and anoxia expansion. The same combination of proxy records (δ^{13} C, δ^{34}S, I/Ca) links Silurian events to ocean anoxia (Young et al., 2019 and Bowman et al., 2020). During the end-Devonian mass extinction (~359 Ma), low I/Ca marked an interval of deoxygenation more expanded than the interval of Hangenberg black shale deposition. The deoxygenation indicated by I/Ca is overall coeval with time intervals of carbon isotope excursion and biotic crisis indicated by fossil evidence (Liu et al., 2020).

The Permo-Triassic (P-T) mass extinction (~252 Ma) is the most severe biotic crisis in the Phanerozoic, during which possibly ~90% of marine species went extinct (Payne et al., 2004). Many lines of evidence, based on biotic proxies as well as organic and inorganic chemical proxies, document pervasive and widespread anoxia and even euxinia during this extinction event (e.g.,

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Algeo et al., 2015; Brennecka et al., 2011; Elrick et al., 2017; Lau et al., 2016; Zhang et al., 2018). An early attempt to use carbonate iodine content as a redox proxy found very low I/Ca values across the P-T boundary, but concluded that these could be attributed to diagenesis (Loope et al., 2013).

6.2 Mesozoic Oceanic Anoxic Events

As a proof-of-concept, the iprOxy was first tested across Mesozoic Oceanic Anoxic Events (OAEs), generally associated with rapid warming and changes in the nutrient cycle, leading to large-scale, low-oxygen conditions in the oceans (Jenkyns, 2010). One iconic signature of OAEs is the positive carbon isotope excursions (CIE), reflecting enhanced global burial of organic matter. Records of the Toarcian OAE (~182 Ma) and the Cenomanian–Turonian OAE 2 (~92 Ma) generally show lower I/Ca during CIEs, as expected during the buildup of widespread reducing conditions in the oceans (Lu et al., 2010). In a follow-up study, carbonate I/Ca records across OAE 2 were obtained from seven sections and compared with Earth system modeling results (Zhou et al., 2015). Upper ocean oxygenation changes were spatially variable, and locally, some deoxygenation developed before the global CIE (Zhou et al., 2015), a scenario supported by trace metal and isotopic data (Owens et al., 2017; Them et al., 2018). I/Ca responded to a brief episode of reoxygenation due to global cooling during the Plenus cold event in the first half of OAE 2 (Zhou et al., 2015).

The I/TOC (total organic carbon) ratios in modern surface-subsurface sediments correlate with bottom water oxygen levels (Kennedy and Elderfield, 1987a, b; Lu et al., 2008; Price and Calvert, 1973). I/TOC records of the OAE 2 consistently show expansion of bottom-water deoxygenation during the CIE and a latitudinal gradient in agreement with ventilation patterns in an Earth system model (Zhou et al., 2017). The sedimentary iodine sink in the global ocean appears to be dependent on the flux of organic matter burial in oxygenation bottom water, since iodate (the oxidized form) is much more efficiently adsorbed onto organic matter than iodide (Zhou et al., 2017). Thus, the degree of global iodine drawdown during OAEs may be limited by iodate reduction in anoxic water lowering the efficiency of iodine adsorption onto organic materials.

OAEs were not generally associated with mass extinctions, possibly due to the presence of well-oxygenated ocean refuges, which may have existed, as suggested by I/Ca data for OAE 2. Alternatively, the seafloor area under anoxic waters may have been smaller than commonly considered (Clarkson et al., 2018). Another possibility is that Mesozoic faunas had greater physiological