

was extremely low in the Archean Eon (>2.5 Ga), and while multiple lines of evidence suggest that Earth's oxygenation was protracted (Kah *et al.*, 2004; Kah and Bartley, 2011; Lyons *et al.*, 2014; Planavsky *et al.*, 2014), pO<sub>2</sub> may have risen abruptly at two different points in time: first during the "Great Oxygenation Event" (GOE) at ~2.4 Ga (Canfield, 2005; Holland, 2006; Guo *et al.*, 2009; Farquhar *et al.*, 2011), when atmospheric O<sub>2</sub> rose from <0.001 % to an intermediate value commonly estimated as 1 to 10 % of the current level (Farquhar *et al.*, 2000; Pavlov and Kasting, 2002), and again during a "Neoproterozoic Oxygenation Event" (NOE) at ~800 to 542 million years ago (Canfield and Teske, 1996; Fike *et al.*, 2006; Frei *et al.*, 2009; Och and Shields-Zhou, 2012). The latter transition may well have continued into the Phanerozoic Eon, eventually resulting in near-present O<sub>2</sub> (Berner, 2006; Dahl *et al.*, 2010; Sperling *et al.*, 2015).

Redox-sensitive major and trace elements in iron formations and black shales deposited beneath euxinic waters have been developed as proxies to reconstruct palaeoenvironmental history in deep time (Scott *et al.*, 2008; Konhauser *et al.*, 2009; Sahoo *et al.*, 2012). The paucity of these facies in many Proterozoic successions, however, limits the continuity of current reconstructions of Earth's oxygenation. Here we provide evidence for the hypothesis that carbonate-based redox proxies can provide an independent estimate of past pO<sub>2</sub>, expanding the palaeoredox record in time and space (Hardisty *et al.*, 2014). Limestone and penecontemporaneous dolomites that retain depositional signatures well (Wilson *et al.*, 2010) are abundant in the geologic record, typically recording shallow marine environments that would have been in open communication with the overlying atmosphere. Palaeoenvironmental research on carbonate rocks commonly focuses on individual stratigraphic successions; here we adopt a complementary strategy, analysing a large suite of Phanerozoic, Proterozoic, and Archean samples that enables us to make statistical statements (Sperling *et al.*, 2015) about Zn/Fe in the global surface ocean through geologic time. More importantly, we develop a new tool to provide quantitative constraints on atmospheric pO<sub>2</sub> through Earth history.

In the modern ocean, zinc input from hydrothermal ridge systems (~4.4 × 10<sup>9</sup> mol yr<sup>-1</sup>) is an order of magnitude greater than riverine fluxes (~3.4 × 10<sup>8</sup> mol yr<sup>-1</sup>; Robbins *et al.*, 2013). As an essential nutrient in many phytoplankton enzymes, especially those of eukaryotes (Williams and da Silva, 1996), zinc plays an important role in marine primary production, and for this reason, Zn is depleted in surface waters relative to the deep sea (Morel and Price, 2003). Zn concentrations in euxinic black shale and iron formations (Robbins *et al.*, 2013; Scott *et al.*, 2013), however, suggest that the bioavailability of Zn has not changed dramatically through Earth history. The Fe budget is similar to that of Zn, wherein hydrothermal input dominates over riverine fluxes by a factor of ~9 (Wheat *et al.*, 2002). Under sulphidic conditions, dissolved Zn<sup>2+</sup> and Fe<sup>2+</sup> behave similarly and are rapidly precipitated as sulphides (Morse and Luther III, 1999). In addition, because both Fe and Zn behave as incompatible elements during mantle partial melting, Zn/Fe has been developed as a tracer of mantle redox, revealing that the oxygen fugacity of the upper mantle has remained relatively constant

## Tracing Earth's O<sub>2</sub> evolution using Zn/Fe ratios in marine carbonates

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### Abstract

Through Earth history, atmospheric oxygen has increased from initial values near zero to its present day level of about 21 % by volume; concomitantly, changes in ocean redox conditions have fundamentally altered global biogeochemical cycles. While there is a reasonable understanding of where oxygen history begins and ends, the quantitative timetable of oxygenation that links the endpoints has proven contentious. Equilibrium between marine surface environments and the overlying atmosphere suggests that carbonate-based redox proxies could refine palaeoredox records in time and space. Here we explore the use of Zn/Fe ratios to infer the evolution of atmospheric O<sub>2</sub> through time, based on marine carbonate rocks that are well characterised in terms of depositional age, environmental setting, and diagenetic history. While Fe and Zn in the shallow ocean are mainly sourced from hydrothermal inputs, their redox sensitivities differ significantly, so that geological intervals with higher O<sub>2</sub> would be characterised by stepped increases in Zn/Fe as preserved in shallow marine carbonates. Therefore, Zn/Fe analyses of ancient carbonates allow us to constrain past atmospheric pO<sub>2</sub> levels, providing a secular record of atmospheric O<sub>2</sub> over the past 3.5 billion years. In particular, we corroborate an earlier proposal that for much of the Proterozoic Eon, O<sub>2</sub> levels were as low as 0.1-1 % of present atmospheric level. We conclude that Zn/Fe in shallow marine carbonate rocks has potential to provide a quantitative tracer for the long-term redox evolution of the oceans and the rise of atmospheric O<sub>2</sub>.

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### Introduction

Earth's O<sub>2</sub>-rich atmosphere, unique among known planets, has played an essential role in evolving feedbacks between life and environment. Atmospheric O<sub>2</sub>

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through Earth history (Lee *et al.*, 2010). In the following discussion, we assume that Zn/Fe in hydrothermal inputs into the ocean have not changed significantly through time. We recognise, however, that a number of factors could limit this assumption, and consider these below.

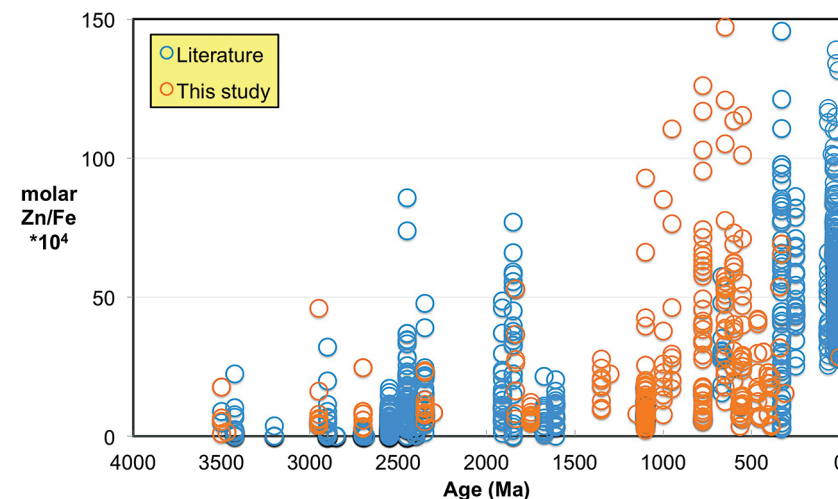
Zn/Fe in the sedimentary record thus has the potential to document Earth surface redox evolution if we consider the following assumptions: 1) Zn and Fe budgets in the oceans are dominated by hydrothermal inputs and are therefore not significantly influenced by secular evolution of continental inputs; 2) Fe<sup>2+</sup> and Zn<sup>2+</sup> have similar solubility in the oceans; 3) the partition coefficient of Zn/Fe ratios into carbonates has remained the same through time; and 4) when Fe<sup>2+</sup> is oxidised to Fe<sup>3+</sup>, it precipitates from seawater and thus is not incorporated into carbonate; zinc, however, remains divalent as Zn<sup>2+</sup>.

## Methods

Major, trace, and rare earth elements (REE) concentrations were determined with a Thermo Scientific® iCAP-Q ICP-MS (Inductively Coupled Plasma – Mass Spectrometry) at the Carnegie Institution of Washington. Approximately 5 to 10 mg of micro-drilled sample powders were weighed and dissolved in 2 ml distilled 0.4 M HNO<sub>3</sub> and reacted for 12 hours. The resulting solutions were centrifuged for 5 minutes at ~6000 rps and 1 ml of the supernatant was pipetted and diluted with distilled 4 ml 0.4 M HNO<sub>3</sub> for elemental analysis. Calibration curves were created using multi-elemental standards with different dilutions made from pure element solutions (Alfa Aesar®). Both standard and sample solutions were doped with 4 ppb In to correct for instrumental drift. Precision of the analyses was determined by repeated analyses of an in-house carbonate standard, and was typically better than 5 % (2σ) for major elements, and better than 10 % (2σ) for most trace elements including REE. Accuracy of the analyses was determined by replicates of an international coral standard (JcP-1), as shown in Figure S-1.

## Results and Discussion

Here, we report Zn/Fe molar ratios in marine carbonate rock through Earth history (Fig. 1) and provide a quantification of atmospheric O<sub>2</sub> evolution since the Mesoarchean Era. Samples (n = 1700) come from our analyses (n = 300), as well as a literature compilation (see SI-1 Table S-1). In all carbonate samples, the potential for diagenetic alteration is of concern. To evaluate the degree of sample alteration, we selected specimens with known sedimentological and stratigraphic context and investigated their petrography and elemental and isotope geochemistry. Samples used in this study were primarily composed of fine-grained limestone and penecontemporaneous, fabric-retentive dolostone, including both micrites and stromatolites. We micro-sampled carbonate specimens from polished billets to avoid weathering alteration, secondary veins/precipitation, and areas with



**Figure 1** Zn/Fe molar ratios versus time for individual carbonate analyses. The figure contains ~1700 measurements of Zn/Fe data, including literature data (blue), and our 300 new analyses (orange).

visible non-carbonate phases. In addition to geological and petrographic criteria, we further selected samples based on primary isotopic and trace element patterns (see SI-2).

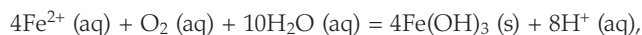
Even if we carefully select the most primary samples, we cannot ignore diagenetic influences on the elemental composition of sampled carbonates, as this can contribute to local variation of Zn/Fe (Fig. 1). Both Zn and Fe partition coefficients ( $K_d$ ) from fluid to carbonates increase with increasing diagenesis as shown by earlier work of Brand and Veizer (1980). Also,  $K_d$  (Fe) increases faster compared to  $K_d$  (Zn), from 1 to 20 and from 5.2 to 5.5 for Fe and Zn, respectively. According to this work, diagenesis will cause a decrease in Zn/Fe ratios by incorporating more Fe than Zn in carbonates. We acknowledge that all of the carbonates examined here have undergone some degree of burial diagenesis, and this will be reflected in the variance of Zn/Fe within individual time intervals. Also, local primary production differences may contribute to Zn/Fe variability of different formations from the same interval. In the modern oxidised shallow ocean, particulate Fe sourced from eroding continents remains biogeochemically labile and may be cycled back to a dissolved phase during diagenesis in reducing continental margin sediments (Raiswell *et al.*, 2006). Therefore, there is also a potentially large and variable source of reactive Fe to shallow marine settings that is decoupled from the Zn flux, which likely causes Zn/Fe ratios to be lower and therefore could contribute to the variations observed in Zn/Fe data. In addition, theoretical calculations suggest that kinetic effects on trace element



partitioning in carbonate may contribute to Zn/Fe variability in samples from the same locality (Watson, 2004; DePaolo, 2011). Importantly, however, these influences should not result in systematic variations that would contribute to observed first-order secular changes. We plot all carbonate samples based on their lithology in Figure S-2; this shows that there is no systematic difference between limestone and dolomite samples through time - not unexpected, as many Proterozoic dolomites formed penecontemporaneously and preserve geochemical signatures as well as coeval limestones that underwent neomorphism during burial.

We observe a distinct trend of increasing Zn/Fe through time (Fig. 1), especially around the GOE and NOE. Our Palaeoproterozoic data are also consistent with earlier suggestions that pO<sub>2</sub> may have risen substantially during the GOE and then declined again to persistent Proterozoic values (Lyons *et al.*, 2014). Employing three statistically complementary approaches (see details in SI-3), carbonate Zn/Fe could follow “step” or “smooth” fits through Earth’s history (Figs. S-3, S-4 and S-5), where we prefer the “step” approach with lognormal distributions (see Figs. 2 and S-3). Using lognormal distributions to estimate Zn/Fe through time, we can provide quantitative constraints on Earth’s atmospheric O<sub>2</sub> evolution, as follows.

From the chemical reaction of Fe oxidation from Fe<sup>2+</sup> to Fe<sup>3+</sup>:



$$K = \frac{a_{(\text{H}^+)}^8}{a_{(\text{H}_2\text{O})}^{10} \times a_{(\text{Fe}^{2+})}^4 \times a_{(\text{O}_2)}}, \quad \text{Eq. 1}$$

where *K* is the equilibrium constant and *a* is activity. In this equation, we assume that when Fe<sup>2+</sup> oxidises to Fe<sup>3+</sup> and is precipitated from the aqueous system as iron hydroxide, and only Fe<sup>2+</sup> gets incorporated into carbonates. We are aware that secular variations in seawater sulphate might modulate hydrothermal iron fluxes through time via the formation of iron sulphides (Kump and Seyfried, 2005), we do not know the extent to which Zn abundances might similarly be buffered and so do not consider this in our first-order model. Assuming O<sub>2</sub> equilibrium between atmosphere and surface ocean on hundred million year time scales, we can write the equation using atmospheric oxygen fugacity, *f*<sub>(O<sub>2</sub>)</sub>, as

$$\log K = 4 \log \frac{1}{a_{(\text{Fe}^{2+})}} - \log f_{(\text{O}_2)} + \log \frac{a_{(\text{H}^+)}^8}{a_{(\text{H}_2\text{O})}^{10}} \quad \text{Eq. 2}$$

if we assume the Zn concentrations in seawater and partitioning of Zn/Fe from seawater to carbonate minerals are constant over Earth history. Therefore, we can write the equation normalised to Zn<sup>2+</sup> as

$$\log K = 4 \log a_{(\text{Zn}^{2+}/\text{Fe}^{2+})}^P - \log f_{(\text{O}_2)}^P + \log \frac{a_{(\text{H}^+)}^8}{a_{(\text{H}_2\text{O})}^{10}} \quad \text{Eq. 3}$$

$$\log K = 4 \log a_{(\text{Zn}^{2+}/\text{Fe}^{2+})}^M - \log f_{(\text{O}_2)}^M + \log \frac{a_{(\text{H}^+)}^8}{a_{(\text{H}_2\text{O})}^{10}}$$

in which superscripts *P* and *M* indicate the past and modern parameters. Assuming pH and *K* are constant (see SI-4), we can simplify the relationship between Fe/Zn ratios and *f*<sub>(O<sub>2</sub>)</sub>, as

$$f_{(\text{O}_2)}^P = r^4 \cdot f_{(\text{O}_2)}^M \quad \text{Eq. 4}$$

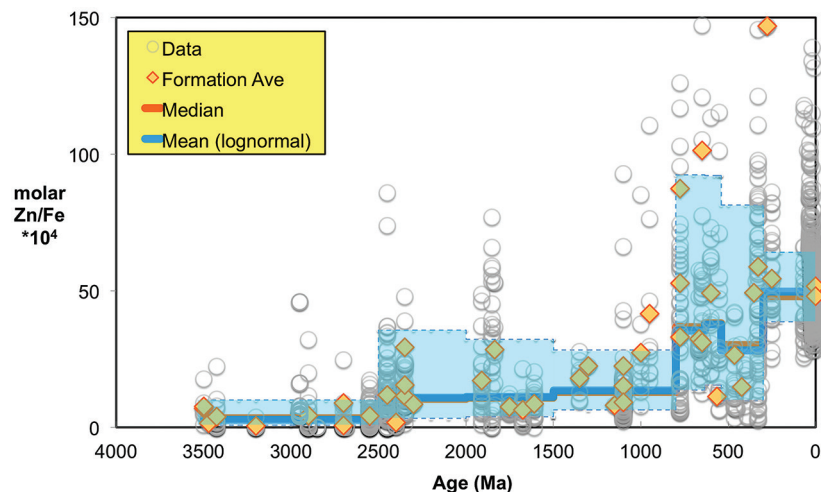
where *f*<sub>(O<sub>2</sub>)</sub><sup>*P*</sup> is the oxygen fugacity in the past (any time in Earth’s history), *f*<sub>(O<sub>2</sub>)</sub><sup>*M*</sup> is the oxygen fugacity in modern time, and

$$r = \frac{(\text{Zn}^{2+}/\text{Fe}^{2+})^P}{(\text{Zn}^{2+}/\text{Fe}^{2+})^M} \quad \text{Eq. 5}$$

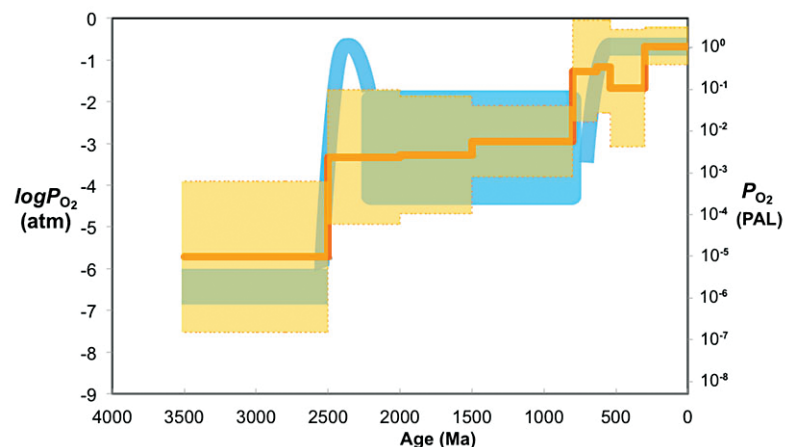
provides Zn/Fe ratios in past carbonate normalised to modern values. If we assume that atmospheric O<sub>2</sub> is in equilibrium with the shallow marine environment, and that we know the current atmospheric pO<sub>2</sub> (0.21) and the modern seawater Zn/Fe ratios as reflected in Zn/Fe ratios of marine carbonates, we can use Zn/Fe to calculate *f*O<sub>2</sub> (also expressed as pO<sub>2</sub> at any given time of Earth history (Fig. 3). This pO<sub>2</sub> curve provides a more continuous coverage of atmospheric O<sub>2</sub> levels compared to compilations derived from multiple geochemical tracers, such as mass-independent S isotopes and palaeosol records (Rye and Holland, 1998; Catling and Claire, 2005).

The *log* pO<sub>2</sub> curve in Figure 3 reproduces what we think we know about oxygen history: estimated pO<sub>2</sub> is extremely low in the Archean and reaches modern levels only in the mid-Palaeozoic Era. Moreover, the estimates match our current understanding (Lyons *et al.*, 2014) of a general two-step increase of atmospheric O<sub>2</sub> around the GOE and the NOE. Importantly, our study provides an estimate of the upper and lower bounds on pO<sub>2</sub> in the mid-Proterozoic atmosphere, with a preferred value between 0.1 and 1 % PAL. This value is substantially lower than traditional estimates based on palaeosol work (Canfield, 1998; Rye and Holland, 1998), but consistent with recent estimates based on an independent tracer, a kinetic model for Cr-Mn oxidation and Cr isotopes in ironstones (Planavsky *et al.*, 2014). We conducted sensitivity tests of temperature and pH variations on our pO<sub>2</sub> estimates and found that the influence of





**Figure 2** Zn/Fe molar ratio versus time for carbonates, averaged by formation. Formation averages (orange diamonds) were calculated based on simple arithmetic mean of samples within the same formation. Median (orange) and mean from lognormal distribution (blue) lines were calculated based on all samples from the designated time intervals. Estimated Zn/Fe ratio curve through Earth's history. Uncertainties (light blue fields) are estimated based on one standard deviation from the lognormal distribution.



**Figure 3** Estimated atmospheric  $pO_2$  through Earth's history. The orange line indicates the best estimate (mean values from lognormal distribution) from carbonate Zn/Fe ratios from this study (yellow fields show the upper and lower range of estimated  $O_2$ , which is calculated based on one sigma of lognormal distributions). The blue field indicates semi-quantitative interpretation from current understanding of the atmospheric  $O_2$  curve (modified from Lyons *et al.*, 2014).

temperature is negligible. pH, however, could potentially lower  $pO_2$  estimates, especially for earlier samples when  $pCO_2$  was high (see SI-4 for details); thus our estimates of Proterozoic  $pO_2$  should be considered conservative and may overestimate past oxygen levels. There are hints of biologically interesting structure in the Neoproterozoic and Cambrian records, but at present our sample numbers and bin sizes are too small to address this in detail. As more carbonate data become available for key transitional time periods such as those around GOE and NOE, potentially complex secular patterns of redox change may become clearer. Further investigations on well-constrained modern and Phanerozoic marine carbonates are currently underway to evaluate with more quantitative rigour the potential effects of diagenesis, mineralogy, and ocean depth gradient distributions on the proxy proposed here.

## Conclusion

In summary, we have demonstrated the potential for using divalent cations in carbonates as sensitive proxies for the evolution of Earth's near surface environment. Because many marine carbonate rocks were deposited in shallow marine environments, in direct contact with the atmosphere, elemental ratios are likely to reflect equilibrium atmospheric conditions extending back to the Archean Eon and including time intervals poorly represented by other lithologies. Although further work will be needed to fully validate this promising palaeoredox proxy, carbonate-based redox proxies show great potential to expand the palaeoredox record and to provide self-consistent and quantitative constraints on atmospheric  $O_2$  through Earth's history.

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## Additional Information

**Supplementary Information** accompanies this letter at [www.geochemicalperspectivesletters.org/article1603](http://www.geochemicalperspectivesletters.org/article1603)



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## Author Contributions

X-ML and RMH designed the project with inputs from all authors. X-ML performed the chemical analyses. X-ML wrote the manuscript with inputs from all authors. LK, AHK, HC, AJK, and RMH provided samples.

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