nature geoscience

LETTERS

| DOI: 10.1038/NGEO1679

Bioavailability of zinc in marine systems through time

Clint Scott[1,2]*, Noah J. Planavsky[1], Chris L. Dupont[3], Brian Kendall[4,5], Benjamin C. Gill[6], Leslie J. Robbins[7], Kathryn F. Husband[8], Gail L. Arnold[9], Boswell A. Wing[2], Simon W. Poulton[8], Andrey Bekker[10], Ariel D. Anbar[4,11], Kurt O. Konhauser[7] and Timothy W. Lyons[1]

The redox state of the oceans strongly influences the concentration of dissolved trace metals in sea water. Changes in the redox state of the oceans are thought to have limited the availability of some trace metals in the past, particularly during the Proterozoic eon, 2,500 to 542 million years ago[1–4]. Of these trace metals, zinc (Zn) is of particular importance to eukaryotic organisms, because it is essential for a wide range of basic cellular functions. It has been suggested[5] that during the Proterozoic, marine environments were broadly euxinic—that is, anoxic and sulphidic—which would have resulted in low Zn availability. Low Zn bioavailability could therefore be responsible for an observed delay in eukaryote diversification[2]. Here we present a compilation of Zn abundance data from black shales deposited under euxinic conditions from the Precambrian time to the present. We show that these values track first-order trends in seawater Zn availability. Contrary to previous estimates[6], we find that Zn concentrations during the Proterozoic were similar to modern concentrations, supporting recent studies[7,8] that call for limited euxinia at this time. Instead, we propose that predominantly anoxic and iron-rich deep oceans, combined with large hydrothermal fluxes of Zn, maintained high levels of dissolved Zn throughout the oceans. We thus suggest that the protracted diversification of eukaryotic Zn-binding proteins was not a result of Zn biolimitation.

There has been extensive discussion about the relative roles of environmental versus biological controls on the evolutionary history of life[9,10]. For instance, it has long been debated[10] whether metazoan divergence and radiation were triggered by an oxygenation event, or reflect the timing of genetic innovation independent of an environmental control. Similar considerations apply to eukaryotic diversification in general. Stem-group eukaryotes emerged in the Archaean eon or the Palaeoproterozoic era, with estimates for emergence ranging from 3,200 to 1,600 Myr ago[11,12]. However, the fossil record indicates that there was limited morphological and functional diversity in eukaryotes before the latest Proterozoic, 800–600 Myr ago[11,12]. Similarly, biomarker work on sedimentary successions indicates very limited eukaryote primary production even in mid-Proterozoic ecosystems[12]. Whether a biological or environmental control was responsible for the 1–2-billion-year delay in the diversification of eukaryotes is a fundamental and unanswered question in the history of life on Earth.

A significant delineation between prokaryotic and eukaryotic life lies in the utilization of the trace element Zn. Eukaryotic proteomes bind substantially more Zn than do prokaryotic proteomes on a proportional basis (that is, percentage of total proteome). Nearly 30% of known Zn-binding protein structures are found exclusively in eukaryotes and account for the entire proportional difference between prokaryotic and eukaryotic Zn-binding proteomes[13]. Phylogenomic reconstructions[2] demonstrate that these protein structures evolved either concurrent with or after the emergence of the Eukaryotic domain. Data on cellular localization show that these proteins are found primarily within the nucleus, the hallmark feature of eukaryotes, and most of these structures are involved in transcriptional, post-transcriptional or translational regulation[2].

A common explanation for the delayed diversification of eukaryotes during the Proterozoic is the development of seawater trace-metal biolimitation under broadly euxinic conditions[1,6] where many elements with an affinity for sulphur (Mo, Zn, Cu and so on) are predicted to have existed at low concentrations (10^{-16} to 10^{-18} M), many of orders of magnitude below modern levels. New models for Proterozoic ocean chemistry call for broadly ferruginous deep oceans and a more limited occurrence of euxinic conditions along productive continental margins[7,8]. As even a limited extent of marine euxinia has the potential to significantly drawdown the global marine inventories of many transition metals[4], it is important to explore the potential for trace metal biolimitation under these less extreme redox conditions. Given the high Zn requirements of eukaryotes, relative to prokaryotes, Zn would be one of the most likely trace metals to provide a geochemical barrier specific to eukaryotic evolution.

The average concentration of Zn in Earth's crust is ~85 ppm (ref. 14), but like many transition metals it is conspicuously enriched in fine-grained, organic-rich sediments and their ancient analogues—black shales[15]—often exceeding 1,000 ppm. Trace-metal enrichments in general, and Zn enrichments specifically, are well known to be derived directly from sea water (for example,

---

[1]Department of Earth Sciences, University of California, Riverside, California 92521, USA, [2]Department of Earth and Planetary Sciences, McGill University, Montreal, Quebec H3A 2A7, Canada, [3]Microbial and Environmental Genomics Group, J. Craig Venter Institute, La Jolla, California 92121, USA, [4]School of Earth and Space Exploration, Arizona State University, PO Box 871404, Tempe, Arizona 85287, USA, [5]Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada, [6]Department of Geosciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA, [7]Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G 2E3, Canada, [8]School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK, [9]Max Planck Institute for Marine Microbiology, 28359 Bremen, Germany, [10]Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada, [11]Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, USA. *e-mail: clintonscott@usgs.gov.

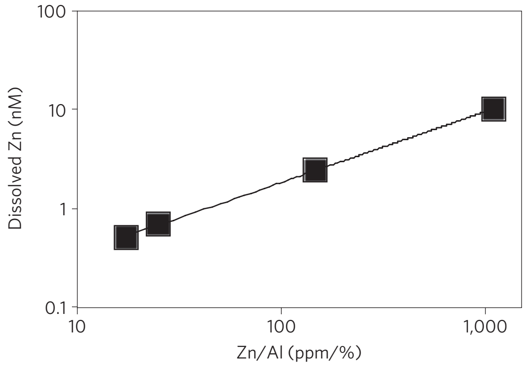

Figure 1 | Average Zn enrichments (Zn/Al ratios) in modern euxinic (anoxic and sulphidic) settings. The magnitude of the Zn enrichment in sediments scales with the dissolved Zn concentration in sea water. This relationship suggests that enrichments in euxinic shales can be used to track the evolution of the marine Zn reservoir in the past. Data, in order of increasing Zn enrichments, are from the Black Sea, Cariaco Basin, Jellyfish Lake and Framvaren Fjord (see Supplementary Information for further information). Analytical error is smaller than the symbols.

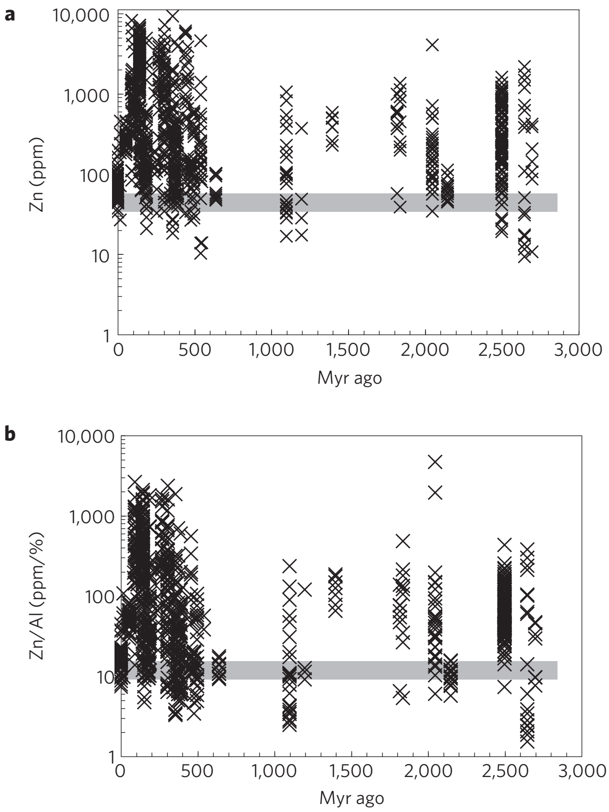

Figure 2 | Zn enrichments in euxinic black shales through time. a, Bulk Zn concentrations. **b**, Zn concentrations normalized to Al concentrations (Zn/Al; ppm/wt %). Grey bars represent the crustal average for Zn concentrations and Zn/Al ratios, respectively[14].

ref.[15]), both in association with phytoplankton biomass and with authigenic sulphide minerals.

Under sulphidic conditions, dissolved Zn is rapidly precipitated, either in solid solution with iron sulphides or as an independent authigenic phase[16]. Importantly, for modern sediments deposited beneath euxinic (anoxic and sulphidic) bottom waters we find a direct correlation between the concentration of Zn in the water column and the magnitude of enrichment in the underlying sediments (Fig. 1). We stress that this is a qualitative relationship, and Zn concentrations in ancient black shales should not be used to make quantitative estimates of seawater Zn concentrations in ancient oceans. However, the first-order relationship between the concentration of Zn in sea water and the magnitude of enrichment in underlying euxinic sediments suggests that sediment Zn enrichments can be used to track first-order shifts in dissolved Zn levels through time. A direct correlation between dissolved concentrations and sediment enrichments under euxinic conditions is also well developed for the transition metal Mo (ref. 17) and has been used to infer temporal trends in seawater Mo inventories[4].

In this study we follow the precedent of ref. 4 and focus on the enrichment of Zn in ancient euxinic black shales as a first-order indicator of changes in the size of the marine Zn reservoir through time. If seawater Zn concentrations were orders of magnitude lower than modern levels during the Proterozoic[6], we should expect Zn enrichments in Proterozoic black shales to be virtually absent, just as Mo enrichments are virtually absent before the rise of atmospheric oxygen[4,18].

We measured Zn concentrations from a large sample set of Precambrian black shales and compared them with published results from Phanerozoic (<542 Myr old) shales and modern sediments (Fig. 2a). Our focus on enrichments in shales deposited under euxinic conditions is intended to exclude data from marine settings where sulphide was restricted to sediment pore waters (that is, where trace-metal enrichments in the sediments do not straightforwardly reflect their dissolved concentrations in the overlying water column). Euxinic shales were identified using well-established palaeoredox proxies[7,8]. Owing to the relatively high background concentration of Zn in continentally derived material, Zn concentrations are also presented normalized to Al to highlight enrichments beyond the detrital flux (Fig. 2b).

As Zn can become enriched in black shales during secondary mineralization, we have avoided known mineralized units and have targeted samples exhibiting depositional or early diagenetic sulphide textures (see Supplementary Information). In contrast, mineralized shales are typically characterized by coarser euhedral sulphides and commonly are conspicuously altered on a macroscopic scale (for example, formation of quartz and sulphide veins). In some cases, later mineralization can be ruled out by the agreement between black shale Re–Os and zircon U–Pb depositional age constraints for the succession (for example, ref. 19).

Our Precambrian sample set includes many previously studied units, including the 2,640-Myr-old Roy Hill Member of the Jeerinah Formation, the oldest known occurrence of euxinia in Earth's history[18], and the 2,500-Myr-old Mount McRae shale, which contains evidence for oxidative processes before the Great Oxidation Event[19]. From the Proterozoic, we present data from several extensively studied units: the about 2,100-Myr-old Sengoma argillite[20], the 1,840-Myr-old Rove Formation[21] and the 1,400-Myr-old Velkerri Formation[22]. In addition, we have analysed black shales from the about 1,100-Myr-old Atar Group of the Taoudeni Basin, Mauritania[23], providing a much-needed addition to the sparse mid-Proterozoic black shale record (for example, refs 3,4). Through careful selection and assembly of large, well-characterized sample and data sets, we have produced a reliable, first-order archive of temporal changes in Zn concentrations in Precambrian and Phanerozoic sea water.

Our record of Zn enrichments in ancient euxinic shales suggests a relatively stable marine reservoir over the past 2,700 Myr, rather than the extreme Zn depletions suggested by previous thermodynamically based models[6]. During this time, the mean Zn/Al ratios (Fig. 2b) for euxinic black shales are typically between 15 and 1,000. We observe no clear trend across the Great Oxidation Event (about 2,300 to 2,500 Myr ago) and only a mild increase in maximum values (and no significant shift in the mean) coincident with late Neoproterozoic surface oxygenation[4,24]. During the Phanerozoic we observe higher maxima, and thus a wider range in enrichments, but average Zn/Al ratios typically remain within an order of magnitude of both modern and Precambrian samples. Extremely Zn-enriched samples—enrichments outside the observed average range—probably represent sediments with either very slow sedimentation rates or a local hydrothermal source of Zn. Importantly, there is a drop in the magnitude of Zn enrichments in shales deposited under euxinic conditions during some Phanerozoic ocean anoxic events despite persistently high sediment sulphide and organic matter concentrations[25]. This conspicuous absence of discernible Zn enrichment in black shales deposited during the peaks of ocean anoxic events is consistent with the expansion of anoxic and sulphidic environments exerting a strong control on the size of the marine Zn reservoir.

Our evidence for a substantial Zn reservoir in Precambrian oceans conforms with recent geochemical evidence of widespread anoxic and Fe-rich (ferruginous) Precambrian deep oceans, with water-column euxinia limited to productive regions along ocean margins and in restricted basins[7,8]. Hydrothermal fluids are strongly enriched in Zn (ref. 26). However, in an ocean with oxic or euxinic deep waters, little Zn will leave proximal hydrothermal settings owing to oxide and sulphide mineral formation, respectively[26,27]. Conversely, in a ferruginous deep ocean with very low sulphide levels, this flux would provide an additional source of the Zn to the photic zone. We propose that the dominance of ferruginous deep oceans, in combination with strong hydrothermal Zn fluxes, maintained relatively high dissolved Zn levels in Precambrian oceans. More broadly, this study provides further evidence for a kinetic, source–sink balance[4] rather than a thermodynamic (mineral solubility)[6] control on the abundance of trace metals in the Earth's early oceans.

Recent studies emphasizing whole-genome-based proteomics argue for continuously increasing Zn utilization in the eukaryotic lineage[2,28] through time. Eukaryotes, in contrast to bacteria and archaea, have increasingly incorporated Zn-binding structures during the last third of their evolutionary history, such that modern bacteria and archaea still use predominantly ancient metal-binding protein structures, whereas eukaryotes employ both early- and late-evolving structures[2,28]. A direct environmental constraint (that is, biological Zn limitation in broadly euxinic Proterozoic oceans) initially seemed the most plausible hypothesis for the protracted evolution of these proteins[2]. However, our geochemical evidence suggests that Precambrian oceans were not severely Zn bio-limited.

The main use for Zn in eukaryotes is in nuclear, probably regulatory, proteins, most notably in transcription factors such as Zn fingers[2]. Thus, the late diversification of Zn-binding proteins and their preferential use in eukaryotes can be simply tied to their utility in nuclear signalling and the late diversification of complex eukaryotic life in Earth's history. The black shale record of Zn enrichments suggests that the history of biological Zn utilization and, more broadly, metallome (metalloproteome) characteristics within specific lineages, mirrors functional requirements and evolutionary contingencies rather than environmental metal availability as previously proposed[29].

Methods

Major- and trace-element concentrations were determined with inductively coupled plasma mass spectrometry at Arizona State University and the University of California, Riverside following a standard multi-acid (HCl–HNO_3–HF) digestion. Accuracy and precision were monitored with duplicate analyses and shale geostandards. Single-run reproducibility was better than 95%. Euxinic samples were identified by iron speciation methods that have been described in detail elsewhere. In short, pyrite sulphur was extracted during a 2 h hot chromous chloride distillation procedure followed by idiometric titration. Pyrite Fe concentrations were calculated assuming a stoichiometry of FeS_2, unless specified. The total reactive Fe pools were determined using either a boiling, concentrated HCl leach[30] or a sequential extraction method[31] using sodium acetate, dithionite and ammonium oxalate. On the basis of duplicate analyses, the reproducibility of sequential Fe extraction measurements is better than 95% and the reproducibility of the HCl leach is better than 90%.

Received 8 June 2012; accepted 23 November 2012;

References

1. Anbar, A. D. & Knoll, A. H. Proterozoic ocean chemistry and evolution: A bioinorganic bridge. *Science* **297,** 1137–1142 (2002).
2. Dupont, C. L., Butcher, A., Valas, R. E., Bourne, P. E. & Caetano-Anollés, G. History of biological metal utilization inferred through phylogenomic analysis of protein structures. *Proc. Natl Acad. Sci. USA* **107,** 10567–10572 (2010).
3. Planavsky, N. *et al.* The evolution of the marine phosphate reservoir. *Nature* **467,** 1088–1090 (2010).
4. Scott, C. *et al.* Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature* **452,** 457–460 (2008).
5. Canfield, D. E. A new model for Proterozoic ocean chemistry. *Nature* **396,** 450–453 (1998).
6. Saito, M. A., Sigman, D. M. & Morel, F. M. M. The bioinorganic chemistry of the ancient ocean: the co-evolution of cyanobacterial metal requirements and biogeochemical cycles at the Archean/Proterozoic boundary? *Inorg. Chim. Acta* **356,** 308–318 (2003).
7. Planavsky, N. J. *et al.* Widespread iron-rich conditions in the Mid-Proterozoic ocean. *Nature* **477,** 448–451 (2011).
8. Poulton, S. W., Fralick, P. W. & Canfield, D. E. Spatial variability in oceanic redox structure 1.8 billion years ago. *Nature Geosci.* **3,** 486–490 (2010).
9. Butterfield, N. J. Macroevolution and macroecology through deep time. *Palaeontology* **50,** 41–55 (2007).
10. Knoll, A. H. & Carroll, S. B. Early animal evolution: Emerging views from comparative biology and geology. *Science* **284,** 2129–2137 (1999).
11. Buick, R. Early life: Ancient acritarchs. *Nature* **463,** 885–886 (2010).
12. Knoll, A. H., Summons, R. E., Waldbauer, J. E. & Zumberge, J. E. in *Evolution of Primary Producers in the Sea* (eds Knoll, A. H. & Falkowski, P.) (2007).
13. Dupont, C. L., Yang, S., Palenik, B. & Bourne, P. E. Modern proteomes contain putative imprints of ancient shifts in trace metal geochemistry. *Proc. Natl Acad. Sci. USA* **103,** 17822–17827 (2006).
14. Rudnick, R. L. & Gao, S. in *Composition of the Continental Crust* (eds Holland, H. D. & Turekian, K. K.) 1–64 (Treatise of Geochemistry, Elsevier, 2003).
15. Algeo, T. J. & Maynard, J. B. Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chem. Geol.* **206,** 289–318 (2004).
16. Morse, J. W. & Luther, G. W. Chemical influences on trace metal-sulfide interactions in anoxic sediments. *Geochim. Cosmochim. Acta* **63,** 3373–3378 (1999).
17. Algeo, T. J. & Lyons, T. W. Mo-total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions. *Paleoceanography* **21,** PA1016 (2006).
18. Anbar, A. D. *et al.* A whiff of oxygen before the great oxidation event? *Science* **317,** 1903–1906 (2007).
19. Scott, C. T. *et al.* Late Archean euxinic conditions before the rise of atmospheric oxygen. *Geology* **39,** 119–122 (2011).
20. Bekker, *et al.* Fractionation between inorganic and organic carbon during the Lomagundi (2.22-2.1 Ga) carbon isotope excursion. *Earth Planet. Sci. Lett.* **271,** 278–291 (2008).
21. Poulton, S. W., Fralick, P. W. & Canfield, D. E. The transition to a sulfidic ocean ~1.84 billion years ago. *Nature* **431,** 173–177 (2004).
22. Arnold, G. L., Anbar, A. D., Barling, J. & Lyons, T. W. Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. *Science* **304,** 87–90 (2004).
23. Rooney, A. D., Selby, D., Houzay, J-P. & Renne, P. R. Re–Os geochronolgy of a Mesoproterozoic sedimentary succession, Taoudeni basin, Mauritania: implications for basin-wide correlations and Re–Os organic-rich sediments systematics. *Earth Planet. Sci. Lett.* **289,** 486–496 (2010).
24. Canfield, D. E., Poulton, S. W. & Narbonne, G. M. Late-Neoproterozoic deep-ocean oxygenation and the rise of animal life. *Science* **315,** 92–95 (2007).
25. Hetlzel, A., Böttcher, M. E., Wortmann, U. G. & Brumsack, H-J. Paleo-redox conditions during OAE 2 reflected in Demerara Rise sediment geochemistry (ODP Leg 207). *Palaeogeogr. Palaeoclimatol. Paleocol.* **273,** 302–328 (2009).
26. German, C. & von Damm, K. in *Treatise on Geochemistry* Vol. 6 (eds Holland, H. D. & Turekian, K. K.) 181–222 (2003).

27. Edmonds, H. R. & German, C. R. Particle geochemistry in the Rainbow hydrothermal plume, Mid-Atlantic Ridge. *Geochim. Cosmochim. Acta* **68,** 759–772 (2004).
28. Decaria, L., Bertini, I. & Williams, R. J. P. Zinc proteomes, phylogenetics and evolution. *Metallomics* **2,** 706–709 (2010).
29. Lawrence, A. D. & Alm, E. J. Rapid evolutionary innovation during an Archaean genetic expansion. *Nature* **469,** 93–96 (2010).
30. Raiswell, R., Canfield, D. E. & Berner, R. A. A comparison of iron extraction methods for the determination of degree of pyritisation and the recognition of iron-limited pyrite formation. *Chem. Geol.* **111,** 101–110 (1988).
31. Poulton, S. W. & Canfield, D. E. Development of a sequential extraction procedure for iron: Implications for iron partitioning in continentally derived particulates. *Chem. Geol.* **214,** 209–221 (2005).

Acknowledgements

C.S. acknowledges the National Science Foundation and the Natural Sciences and Engineering Research Council. N.J.P. acknowledges a National Science Foundation Graduate Research Fellowship. C.L.D. was supported by a NASA Astrobiology Institute Director's Discretionary Fund. B.K. and B.C.G. acknowledge the National Science Foundation and the Agouron Institute. G.L.A., A.D.A. and T.W.L. acknowledge the NASA Astrobiology Institute and the National Science Foundation. A.B., B.A.W., L.J.R. and K.O.K. acknowledge the support of the Natural Sciences and Engineering Research Council. R. Creaser is thanked for Black River dolomite samples. The National Environment Research Council is acknowledged by S.W.P. for financial support through the Life Science and the Planet Scheme and K.F.H. for a PhD DTA.

Author contributions

C.S. and N.P.J. designed the study. All authors were involved in the interpretations, and writing of this study. C.S., N.P.J., G.L.A., B.K. and K.F.H. analysed samples. B.C.G. compiled Phanerozoic data.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to C.S.

Competing financial interests

The authors declare no competing financial interests.