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**Low oxygen waters limited habitable space for early animals**

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18 The oceans at the start of the Neoproterozoic Era (1000-541 million years ago, Ma) were dominantly anoxic, but may have become progressively oxygenated, coincident with the rise of animal life. However, the control that oxygen exerted on the development of early animal ecosystems remains unclear, as previous research has focussed only on the identification of fully anoxic or oxic conditions, rather than intermediate redox levels. Here, we report anomalous cerium enrichments preserved in carbonate rocks across bathymetric basin transects from nine localities of the Nama Group, Namibia (~550-541 Ma). In combination with Fe-based redox proxies, these data suggest that low oxygen conditions occurred in a narrow zone between well-oxygenated surface waters and fully anoxic deep waters. Although abundant in well-oxygenated environments, early skeletal animals did not occupy
oxygen impoverished regions of the shelf, demonstrating that oxygen
availability (likely >10 μM) was a key requirement for the development of
early animal-based ecosystems.

Geochemical proxies based on Fe-S-C and trace metal systematics have been widely
used to reconstruct the progressive oxygenation of the oceans during the
Neoproterozoic and Cambrian\textsuperscript{1-7}. Accumulating evidence indicates that the deep
oceans were dominantly anoxic and ferruginous (Fe-containing) throughout most of
the Precambrian, with euxinic (sulphidic) mid-depth waters prevalent along
continental margins from \sim 1.8 to 1.0 billion years ago (Ga)\textsuperscript{1,6,8}. From \sim 1.0 to 0.58
Ga, however, euxinic mid-depth waters became less prevalent and ferruginous
conditions expanded, with oxic conditions still largely restricted to surface
waters\textsuperscript{1,8,9}. The oxygenation of the deeper marine realm was both protracted and
spatially heterogeneous, with some marine basins recording persistent deep-water
oxygenation from \sim 580 Ma, whereas regional anoxia remained a feature of some
deeper shelf environments into the Cambrian, \sim 520 Ma\textsuperscript{4,5,7,10} and beyond.

The course of Neoproterozoic oxygenation, and cause and effect associations with
the appearance of animals, remains controversial\textsuperscript{4,11-13}. While modern soft-bodied
sponge-grade animals may tolerate oxygen concentrations as low as 1.25-10 μM\textsuperscript{15},
new innovations in the late Ediacaran, such as motility\textsuperscript{16}, the rise of predation, and
skeletonisation\textsuperscript{17-19}, are all hypothesised to have required higher levels of oxygen\textsuperscript{20}.
However, the oxygen demands of early animals are unconstrained, and observations
from modern biota cannot necessarily be applied to early animals of unknown affinity. Furthermore, while soft-bodied and skeletal Ediacaran fauna dominantly occur in sediments interpreted to have been deposited from oxic waters, fossil occurrences have also been reported in sediments characterised by anoxic geochemical signals\textsuperscript{5,14}. In the latter case, this may be because some early complex organisms were able to colonise habitats during fleeting periods of oxia (such short-lived oxygenation is difficult to detect by geochemical proxies that tend to integrate relatively long periods of time). In both of the above cases, however, there is uncertainty as to whether early animal evolution occurred under fully oxygenated conditions, or whether intermediate redox conditions were more prevalent, which by extension suggests that the oxygen requirements of more complex organisms were lower\textsuperscript{3,15}. An in-depth understanding of these links is currently hampered, however, by the inability of most redox proxies to distinguish between fully oxygenated and intermediate redox states, including nitrogenous or manganous conditions, which may overlap with low concentrations of oxygen\textsuperscript{16,17}. Indeed, it is possible that ‘oxic’ horizons identified through Fe and trace element geochemistry may in fact have formed under low oxygen conditions (but not fully anoxic), at levels insufficient to support diverse skeletal animal communities.

In oxic environments, Ce(III) is oxidised to insoluble Ce(IV) and preferentially scavenged relative to the rest of the rare earth elements and yttrium, REY\textsuperscript{18}. The standard reduction potential of Ce(IV) (+1.61\textdegree V) is closer to Mn(IV) (+1.23\textdegree V) than Fe(III) (+0.77\textdegree V), and Ce oxidation is catalysed on the surface of Mn
Therefore, the redox cycling of Ce in seawater is closely related to Mn(II)/Mn(IV) transformations, which occur at a higher redox potential than the Fe(II)/Fe(III) couple, and hence Mn cycling is more sensitive to intermediate redox conditions. Ce anomalies ($Ce_{SN}/Ce^*_{SN}$) are calculated here based on relative enrichments or depletions in shale-normalised Ce ($[Ce]_{SN}$) compared to neighbouring non-redox sensitive REY:

$$Ce_{SN}/Ce^*_{SN} = \frac{[Ce]_{SN}}{([Pr]_{SN})^2/([Nd]_{SN})}$$

Due to the accumulation of Ce(IV) on the surface of Mn (oxyhydr)oxides, oxic seawater becomes Ce-depleted and exhibits a negative Ce anomaly ($<0.9$) (see Methods and Supplementary Information for discussion of Ce/Ce* thresholds). These Mn (oxyhydr)oxides may be buried intact in sediments beneath oxic bottom waters, or may dissolve in the water column if they encounter low oxygen waters, releasing excess Ce. Therefore, waters beneath the Mn(IV)/Mn(II) redoxcline commonly exhibit a positive Ce anomaly ($>1.3$). Positive Ce anomalies have been recorded alongside Mn enrichments in some modern waters, including Lake Vanda, Antarctica ($Ce_{SN}/Ce^*_{SN}$ up to 2.3, Fig 1), in anoxic brines in the eastern Mediterranean ($Ce_{SN}/Ce^*_{SN}$ up to 2.43, Fig 1), and in the deep-marine Cariaco Basin ($Ce_{SN}/Ce^*_{SN}$ up to 1.21).

Water column REY, and associated Ce anomalies, are thought to be preserved in non-skeletal carbonate rocks without fractionation. Carbonate-bound REY are relatively robust to diagenetic alteration and dolomitisation, but any alteration...
of the Ce anomaly can be identified using non-redox sensitive REY anomalies, such as the Y/Ho ratio, which would also be altered away from seawater patterns\textsuperscript{25,26}. We use a sequential dissolution method that targets REY in the carbonate phase, preventing contributions from sedimentary (oxyhydr)oxides or clays\textsuperscript{26}, which would carry a non-seawater signature. The majority of samples are very pure calcites with low siliciclastic components, but where samples are partially dolomitised they have been treated differently during leaching\textsuperscript{26}. The resulting REY data have been screened for traditional seawater features (Y/Ho ratios >67), and samples with evidence for diagenetic alteration or contributions from non-carbonate phases have been excluded from the presented Ce/Ce\* data (see Methods and Supplementary Information).

We additionally utilise redox interpretations based on published Fe speciation data for these carbonate samples\textsuperscript{5}. Fe-speciation distinguishes anoxic from oxic water column conditions through enrichments in highly reactive Fe (Fe\textsubscript{HR}) relative to total Fe (Fe\textsubscript{T})\textsuperscript{1,27}. Anoxic enrichments in Fe\textsubscript{HR} occur due to the water column formation of either pyrite under euxinic conditions\textsuperscript{27}, or non-sulphidized Fe\textsubscript{HR} minerals (such as Fe oxides or carbonates) under anoxic ferruginous conditions\textsuperscript{1} (see Methods). Although originally calibrated for siliciclastics\textsuperscript{1,27}, enrichments in Fe\textsubscript{HR}/Fe\textsubscript{T} can also be identified in carbonates deposited under anoxic water column conditions\textsuperscript{28}. These Fe\textsubscript{HR} enrichments can far exceed Fe\textsubscript{HR} contents expected under normal oxic deposition, where trace amounts (~0.1 wt%) of Fe may be incorporated into carbonates, or precipitate as Fe-Mn coatings\textsuperscript{28}. However, while early dolomitisation
in shallow burial environments does not generally cause a significant increase in
Fe_{HR}. Late stage deep burial dolomitisation may significantly increase Fe_{HR}, but there
is no petrographic evidence for deep burial dolomitisation in our samples\textsuperscript{5,29}.

Consistent with a recent calibration\textsuperscript{28}, we have limited the application of Fe-
speciation to carbonate samples with >0.5wt% Fe\textsubscript{T}, which buffers against the impact
of non-depositional enrichments in Fe\textsubscript{HR}\textsuperscript{28}. In addition, however, we stress that all of
our redox interpretations based on Fe speciation in carbonates are entirely
consistent with data for interbedded siliciclastics\textsuperscript{5}.

Results

In the present study, we measured REY in 259 carbonate rocks of the Nama Group
from nine sites across two basins. The succession was deposited \textasciitilde550-541 Ma
broadly coincident with the first appearance of skeletal animals\textsuperscript{29-31}, as well as trace
fossil evidence for motility\textsuperscript{32} and soft-bodied fossils belonging to the Ediacaran
biota\textsuperscript{33}. Our samples cover a range of palaeo-depths from shallow inner ramp to
deeper outer ramp waters, in the Kanies, Omkyk and Hoogland Members of the
Kuibis Subgroup, and the Spitzkopf and Feldschuhorn Members of the upper
Schwarzrand Subgroup\textsuperscript{5,29} (Fig 2; see Supplementary Information for full details of
the geological setting). We focus on the first known skeletal animals, Cloudina, a
globally distributed eumetazoan of possible cnidarian affinity\textsuperscript{30,34,35}; Namacalathus,
interpreted as a stem group eumetazoa\textsuperscript{36} or triploblast lophophorate\textsuperscript{37} and
reported from multiple localities; and Namapoikia, an encrusting possible cnidarian
or poriferan known only from the Nama Group\textsuperscript{31}. 
In the Nama Group, the majority of REY distribution patterns are smooth and show a flat or light REY-depleted shape on shale-normalised plots, positive La anomalies, low total REE concentrations, and superchondritic Y/Ho ratios (>67), all of which indicate preservation and extraction of original seawater signals (see Supplementary Information for a description of all data). Four samples exhibit negative Ce anomalies (<0.9) (Fig 2), consistent with an oxic water column interpretation obtained for these samples from Fe-speciation<sup>5</sup>. Ce anomalies are, as expected, absent from the persistently anoxic and ferruginous deepest water setting<sup>5</sup> (Fig 2). Significant positive Ce anomalies (1.30 - 2.15) are, however, prevalent in inner ramp sections in both sub-basins (64 samples). In six cases, positive Ce anomalies are associated with anoxic ferruginous signals, and in one case, a positive Ce anomaly is associated with a sample that gives a robust oxic Fe<sub>HR</sub>/Fe<sub>T</sub> signal. However, for the majority of samples (~90%), Fe<sub>T</sub> was <0.5 wt%, preventing a robust evaluation of water column redox conditions from Fe speciation alone. In these cases, samples have elevated Mn/Fe ratios (median = 0.39), when compared to samples with no positive Ce anomalies (median = 0.14) and anoxic ferruginous samples (median = 0.10), which provides an independent constraint on water column redox conditions, as discussed below (Fig 3).

The regionally widespread positive Ce anomalies across the Zaris and Witputs Basins of the Nama Group imply a surplus of Ce sustained by a rain-down of Mn (oxyhydr)oxides from shallow oxygenated surface waters, and this is supported by
the elevated Mn/Fe ratios of these samples (Fig 3). Redox cycling of Mn (oxyhydr)oxides across the Mn(IV/II) redoxcline would leave ambient waters locally enriched in the Ce released during Mn(IV) reduction (Fig 1). We therefore interpret positive Ce anomalies (>1.3) to indicate intermediate manganous conditions. Where there is an absence of both positive Ce anomalies and any indication of enrichment in Fe (i.e., Fe$_{HR}$/Fe$_T$<0.22 or Fe$_T$<0.5 wt%), we suggest that bottom waters were likely well-oxygenated (which is consistent with Fe$_{HR}$/Fe$_T$ signals in interbedded siliciclastics$^5$), thus preventing the onset of both Fe and Mn reduction. Where data are equivocal (e.g., Fe$_{HR}$/Fe$_T$ between 0.22-0.38 and no Ce anomaly), we are unable to interpret redox conditions.

The outer ramp was persistently anoxic and ferruginous (Brak section) and animals are absent from these settings$^5$ (Fig 4). The deep inner-ramp sections show periods of anoxic ferruginous, manganous and well-oxygenated conditions (Zebra River and Omkyk sections). In these settings, animals are notably absent from ferruginous and manganous waters, whereas well-oxygenated waters support abundant skeletal animals, up to 35 mm in diameter, and adjacent localities show trace fossil evidence for motility$^{32}$. The shallowest inner ramp sections show high-frequency temporal fluctuations between anoxic ferruginous, manganous and well-oxygenated conditions (Zwartmodder, Arasab and Grens sections), as might be expected due to fluctuations in the depth of the chemocline (Fig 4). At Zwartmodder, skeletal animals are present in thin beds$^5$, but there is only one skeletal horizon at Grens, and no animal fossils at Arasab.
In contrast to these ecologies, the Driedoornvlage pinnacle reef grew within a transgressive systems tract in a mid-ramp position, which was persistently well-oxygenated and hosts some very large skeletal animals\textsuperscript{5,31} (up to 1 m) and complex reef-building ecologies\textsuperscript{30}. In the younger Schwarzrand Subgroup, which extends close to the Ediacaran-Cambrian Boundary (~547-541 Ma), there is evidence for persistent well-oxygenated conditions\textsuperscript{5} and mid-ramp Pinnacle Reefs host mixed communities of large and small skeletal animals. At Swartpunt, abundant burrows and soft-bodied biota occur in siliciclastic horizons, where Fe speciation indicates oxic conditions\textsuperscript{5}, while small \textit{in-situ} skeletal animals are found in carbonate rocks throughout the succession\textsuperscript{5}.

Discussion

Our geochemical and palaeontological data demonstrate a striking relationship between the precise redox condition of the water column and the presence and abundance of evidence for animal life. Constraints from the modern open ocean suggest that dissolved Mn(II), and therefore Ce(III), can start to build up in low concentrations in oxic waters with dissolved O\textsubscript{2} <100 \mu M\textsuperscript{17}. However, manganous conditions, whereby Mn becomes the dominant redox buffer, are achieved at lower oxygen concentrations. Reduced Mn can remain stable in the presence of up to 10 \mu M O\textsubscript{2}\textsuperscript{16,38}, although Mn oxidation has been reported locally at lower O\textsubscript{2} concentrations where oxidation is catalysed by enzymatic processes\textsuperscript{39}. Thus, active Mn cycling can occur in anoxic waters, but is commonly documented in partially oxic
waters with at least 10 μM O₂ (and up to 100 μM O₂; Fig 1)\textsuperscript{16,38,40,41}, which represents significant oxygen depletion in comparison to modern fully oxygenated surface waters (~250 μM O₂). The reduction potential for Ce is higher than that for Mn, and so the 10 μM O₂ constraint for manganous waters may represent a lower limit on Ce cycling, as sufficient O₂ to oxidise both Ce and Mn is required for the formation of Ce anomalies.

Our multi-proxy approach allows us to distinguish between fully anoxic and intermediate waters, which contained low but significant amounts of oxygen. Where Fe-speciation in Ce enriched samples gives a robust anoxic signal (Fe\textsubscript{HR}/Fe\textsubscript{T} >0.38), Mn reduction may have persisted, but conditions must have been fully anoxic. However, the majority of samples interpreted to be manganous have insufficient Fe\textsubscript{T} for Fe-speciation (with 85% of these falling below 0.25 wt% Fe\textsubscript{T}, and 35% falling below 0.1 wt% Fe\textsubscript{T}). Even very low oxygen concentrations (nM) are sufficient to prevent highly reactive Fe enrichments, and so the low Fe\textsubscript{T} in shallower environments across the Nama Group may be indicative of oxic conditions\textsuperscript{42}, and this is supported by persistent oxic Fe\textsubscript{HR}/Fe\textsubscript{T} ratios obtained from interbedded siliciclastics in some sections\textsuperscript{5}. We therefore suggest that the manganous zone occurred between well-oxygenated surface waters and deeper anoxic, ferruginous waters, commonly overlapping with low but significant concentrations of oxygen (at least ~10 μM) (Fig 1).
Oxygen exerts an important control on ecosystem structure in modern environments, whereby low oxygen environments are inhabited by smaller animals often lacking skeletons and forming low diversity communities with simple food webs. In general, skeletons are absent from modern oxygen minimum zones when $O_2$ drops below 13 $\mu$M, and large animals are often absent below 45 $\mu$M [refs 44,45]. However, the importance of oxygen in supporting early animal ecosystems as they became increasingly complex in form, metabolic demand, and behaviour through the Ediacaran Period is currently unresolved. In the Nama Group the majority of small skeletal animals (>75%), and all evidence for large skeletal animals, motility, soft-bodied biota and complex ecologies, are found in sediments deposited from well-oxygenated waters (Fig 4). The identification of low-oxygen, manganous water column conditions thus provides a compelling explanation for the general absence of biota in these settings, and implies that poorly oxygenated conditions were insufficient to meet the relatively high oxygen requirements of these early skeletal animals. If we take an upper $O_2$ limit for Mn and Ce reduction of 10 $\mu$M $O_2$, this suggests that Mn-enriched waters could theoretically support small, soft-bodied animals, such as sponges. In contrast, the absence of skeletal animals in Mn-enriched waters is consistent with the high energetic cost of skeletonisation. Possible biomarkers for sponge animals appear in the fossil record at >635 Ma [Ref 46], but it is possible that the availability of well-oxygenated habitats was necessary to support the later appearance of skeletonisation, at ~550 Ma. However, it is also unlikely that reaching an oxygenation threshold alone is sufficient to explain the appearance of skeletons, and many have argued that the
trigger for the rise of skeletonisation may have been ecological, such as the rise of predation\textsuperscript{36,48}.

Our approach highlights that intermediate redox conditions were probably widespread in the Ediacaran ocean, but have not previously been appreciated due to the inability of most commonly used proxies to identify such conditions. Our data suggest that low oxygen water column conditions were insufficient to support early skeletal and reef-building animals, and so the extent of suitable habitat space may have been less than previously identified. The widespread radiation of skeletal animals during the subsequent Cambrian explosion may have been facilitated by a global rise in the extent of habitable, oxygenated seafloor\textsuperscript{7}, alongside other genetic and ecological factors. Our data therefore yield new insight into the debate on the role of oxygen in early animal evolution, suggesting that well-oxygenated waters were necessary to support the appearance of the skeletal animals and complex ecologies that are typical of the terminal Neoproterozoic.
1. Poulton, S. W. & Canfield, D. E. Ferruginous Conditions: A Dominant Feature of


3. Planavsky, N. J. *et al.* Low Mid-Proterozoic atmospheric oxygen levels and the


5. Wood, R. A. *et al.* Dynamic redox conditions control late Ediacaran ecosystems in


7. Chen, X. *et al.* Rise to modern levels of ocean oxygenation coincided with the


   global transition to ferruginous conditions in the early Neoproterozoic oceans.

10. Sperling, E. A. *et al.* Statistical analysis of iron geochemical data suggests limited


25. Tostevin, R. *et al.* Effective use of Ce anomalies as a redox proxy in carbonate dominated marine settings. (accepted).


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**Author contributions**

RAW, ARP, KHH, RT, AMP, FB, and AC collected the samples. MOC, RT, AMP and FB prepared the samples. RT conceived the project and analysed the samples. RT interpreted the Ce anomaly data, after discussions with GAS, TH, RG and SWP. RT wrote the paper, with significant input from GAS, SWP, RAW, and RG.

**Figure 1**

Schematic representation of redox zones and associated geochemical signals in the Zaris Basin, Nama Group during a highstand systems tract. Positive Ce anomalies form as Mn (oxyhydr)oxides dissolve in the manganous zone, and Fe enrichments form under anoxic ferruginous conditions. 10 μM is an estimate of maximum O$_2$ concentrations in the manganous zone, but overlying well-oxygenated waters may have contained higher O$_2$ concentrations. Representative REY patterns, including positive Ce anomalies (magnitude in brackets), are shown for the Omkyk section in
the Nama Group, alongside manganous zones from two modern environments\textsuperscript{20,22} (modern water column data plotted as [REY] $\times 10^6$ to be comparable with sedimentary [REY]).

\textbf{Figure 2}

The location of nine sections within the Kuibis and Schwarzrand Subgroups of the Nama Group is shown on a simplified geological map of Namibia (top left), as well as on a schematic cross section indicating average relative water depth (bottom). Fe\textsubscript{T} data for each location is shown for carbonate and siliciclastic rocks, colour coded for redox interpretation based on Fe\textsubscript{HR}/Fe\textsubscript{T} and Fe\textsubscript{T}\textsuperscript{5}, alongside $C_{eSN}/C_{eSN}^*$ data, screened for carbonate rocks showing seawater REY patterns (e.g. molar Y/Ho>67). Blue Fe\textsubscript{T} data indicate where Fe speciation would predict oxic conditions\textsuperscript{5}, and positive Ce anomalies indicate where oxic waters are interpreted to have been manganous. The presence of \textit{in situ} biota is noted by grey lines\textsuperscript{5}.

\textbf{Figure 3}

Mn/Fe ratios for samples identified as manganous (positive Ce/Ce* and low Fe\textsubscript{T} or oxic Fe-speciation signals), ferruginous (anoxic Fe-speciation signals) and oxic (oxic Fe-speciation signals, no positive Ce anomaly). Mn/Fe is enriched in manganous samples compared with global carbonate (0.29)[Ref 49]. Bars represent median values. Red o\textsuperscript{shes indicate dolomitisised samples.}
Figure 4

A comprehensive redox interpretation is shown for each of the nine localities in the Nama Group, determined using combined Fe and Ce signals (see inset table). *In situ* fossils (grey lines), and local ecologies and general ecology from the literature are shown alongside local water column redox conditions. The bar chart plots the frequency that different biota are found in each redox zone. Large skeletal fossils and burrows are found exclusively in well-oxygenated settings, and small skeletal fossils are largely restricted to well-oxygenated conditions, but may occur where conditions were only fleetingly oxic.

Figure 1

![Diagram showing redox zones and biota distribution](image)

Figure 2

![Diagram showing Ce and Mn distribution](image)
**Figure 3**

- **Carbonate rocks**
  - $\text{Fe}_{\text{HR}}/\text{Fe}_T < 0.22$ (oxic)
  - $\text{Fe}_{\text{HR}}/\text{Fe}_T > 0.38$ (anoxic)
  - No or negative anomaly (<1.3)
  - Positive anomaly (equivocal)($>$1.3)

- **Siliciclastic rocks**
  - $\text{Fe}_{\text{HR}}/\text{Fe}_T$
  - Animal fossils with in situ geochemistry

- **Global carbonates**
  - $\text{Mn/Fe}$
  - Ferruginous
  - Manganous
  - Well-oxygenated

- **OSIS RIDGE**
  - North
  - South

- **Basin mid-ramp**
  - Storm wave base
  - Fair weather wave base

- **Zaris Basin**
  - Kibi Subgroup
  - Schwarzrand Subgroup

- **Witputs Basin**
  - Schwartmodder inner ramp
  - mid ramp
  - outer ramp

- **Zwartmodder**
  - Zebra River
  - Spitzkopf

- **Omkyk**
  - Spitzkopf

- **Mooifontein**
  - Zebra River

- **Feldschuhorn**
  - Brak

- **Swartpunt**
  - Pinnacle Reefs

- **~550 Ma**
  - ~547 Ma
  - ~541 Ma
Figure 4
Methods

Samples from nine shelf-to-basin sections within the Zaris and Witputs basins of the Nama Group encompass a range of palaeo-depths from outer- to inner-ramp settings. Stratigraphic correlations are well-established based on sequence boundaries and ash beds. Unweathered samples were selected, and powdered or drilled avoiding alteration, veins or weathered edges. For Zebra River section, powders were drilled from thin section counterparts, targeting fine grained cements. Carbonate rocks in the Nama Group are very pure, but they have all undergone pervasive recrystallisation. Less than 15% of the samples in this study are dolomitised, and there is no petrographic evidence for deep burial dolomitisation in the Nama Group. Most carbonate rocks are associated with low Mn/Sr ratios and heavy δ¹⁸O (see Supplementary information). The presence of different forms of skeletal biota, soft-bodied biota, trace fossils are reported for precise horizons where geochemical analyses have been performed, indicated by grey lines on Figs 2 and 3. General local ecology, supported by additional information from the literature, is also marked, without associated grey lines. Our sampling focused on carbonates, and hence skeletal fossils are over-represented compared with soft-bodied biota and trace fossils. We define ‘large’ skeletal animals as >10 mm in any dimension, which includes Cloudina hartmanae, some Namacalathus, and Namapoikia.

Rare earth elements
Rare earth elements and yttrium (REY) have a predictable distribution pattern in seawater, and non-biological carbonate rocks should preserve local water column REY at the sediment-water interface\textsuperscript{23}. Ce anomalies develop progressively, but cut-off values are established to define negative and positive anomalies. We define a negative anomaly as $\frac{Ce_{SN}}{Ce_{SN}^*} < 0.9$, consistent with previous work\textsuperscript{51}. A positive anomaly, using the same reference frame, would be defined as $\frac{Ce_{SN}}{Ce_{SN}^*} > 1.1$. But since positive anomalies are not previously described from carbonate sediments, we cautiously use a higher cut off, $\frac{Ce_{SN}}{Ce_{SN}^*} > 1.3$, to ensure any positive anomalies are environmentally significant with respect to positive anomalies recorded from some modern manganous waters (1.21-2.43) (see supplementary information for discussion of $\frac{Ce_{SN}}{Ce_{SN}^*}$ cut-offs). While positive or negative Ce anomalies in carbonate rocks likely represent seawater redox conditions, the absence of any Ce anomaly (0.9-1.3) is somewhat equivocal, and could result from anoxic water column conditions, or overprinting of any Ce anomaly during diagenesis or leaching\textsuperscript{26}. Alternately, Ce anomaly formation may be disrupted in surface waters because of wind-blown dust or photo-reduction of Mn oxides\textsuperscript{52}. Fe (oxyhydr)oxides may also be REY carriers, but do not contain the clear Ce enrichments observed in Mn (oxyhydr)oxides (see Supplementary Information for full discussion of REY carriers).

Diagenetic phosphates, Fe and Mn (oxyhydr)oxides, organic matter and clays can potentially affect the REY signatures of authigenic sedimentary rocks if they are partially dissolved during the leaching process\textsuperscript{53-56}. Care has been taken to partially
leach samples, to isolate the carbonate phase without leaving excess acid, which
may leach contaminant phases (see Ref 26 for detailed discussion of methodology).
Powdered calcite samples were cleaned in Milli-Q water and pre-leached in 2%
nitric acid to remove adsorbed and easily exchangeable ions associated with clay
minerals. The remaining sample was partially leached, also in 2% (w/v) nitric acid,
to avoid contributions from contaminant phases such as oxides and clays. The
supernatant was removed from contact with the remaining residue, diluted with 2%
nitric acid and analysed via inductively coupled plasma mass spectrometry in the
Cross-Faculty Elemental Analysis Facility, University College London. This leaching
method has been designed to extract the carbonate bound REY pool without
contributions from (oxyhydr)oxides or clays. These same leachates were also
analysed for major element concentrations (Mg, Fe, Mn, Al and Sr) via inductively
coupled plasma optical emission spectrometry. Oxide interference was monitored
using the formation rate of Ce oxide, and the formation of 2+ ions was monitored
using Ba$^{2+}$. All REY concentrations were normalised to post-Archean Australian
Shale (PAAS). Ce anomalies were calculated using equation (1).
Standard solutions analysed after every ten samples were within 5% of known
concentrations. Replicate analyses on the ICP-MS give a relative standard deviation
<5% for most trace elements, with a larger standard deviation for the heavy REE
that sometimes have non-normalised concentrations <0.5 ppb. Carbonate standard
material CRM 1c was prepared using the same leaching procedure as the samples,
and repeat analyses give a relative standard deviation <5% for individual REY
concentrations, and calculated Ce anomalies (average=0.80) give a relative standard deviation <3%.

Mn/Sr ratios are <1 for the majority (97%) of samples, and δ¹⁸Ocarb is >-10‰, indicating minimal open-system elemental and isotopic exchange during diagenesis, and excluding deep burial dolomitisation (Fig S3). Ce anomaly data are only presented for carbonates that preserve seawater REY features (smooth patterns with molar Y/Ho>67)²³,²⁶ indicating they originate from the carbonate portion of the whole rock, without contributions from detrital or oxide phases. For samples with Y/Ho>67, 85% also have ΣREE <2 ppm, and all have ΣREE <10 ppm. La anomalies, and small positive Eu and Gd enrichments, are prevalent in samples with Y/Ho>67. Positive Ce anomalies are associated with low Mn/Sr ratios (<1) and low Al, Zr, Ti, Fe and Mn contents in the leachate (<0.2 wt% for Fe, and <500 ppm for Mn), indicating minimal contamination due to diagenetic exchange, leaching of clays or Fe-Mn (oxyhydr)oxide phases (see Supplementary Information for a full assessment of data quality).

Fe speciation

The Fe speciation method quantifies Fe that is (bio)geochemically available in surficial environments (termed highly reactive Fe; Fe₉⁹) relative to total Fe (Fe₇). Mobilisation and subsequent precipitation of Fe in anoxic water column settings results in Fe₉⁹ enrichments in the underlying sediment. The nature of anoxia (i.e. sulphide-rich or Fe-containing) is determined by the extent of sulphidation of the
highly reactive Fe pool$^1$. Fe speciation data for carbonate rock samples discussed here, and accompanying interbedded siliciclastic rocks, come from previously published data$^5$. The Fe-speciation technique was performed using well established sequential extraction schemes$^{29}$. The method targets operationally defined Fe pools, including carbonate-associated-Fe (Fe$_{\text{Carb}}$), ferric oxides (Fe$_{\text{Ox}}$), magnetite (Fe$_{\text{Mag}}$), pyrite Fe (Fe$_{\text{Py}}$) and Fe$_T$. Fe$_{\text{HR}}$ is defined as the sum of Fe$_{\text{Carb}}$ (extracted with Na-acetate at pH 4.5 and 50°C for 48h), Fe$_{\text{Ox}}$ (extracted via Na-dithionite at pH 4.8 for 2h), Fe$_{\text{mag}}$ (extracted with ammonium oxalate for 6h) and Fe$_{\text{py}}$ (calculated from the mass of sulphide extracted during CrCl$_2$ distillation). Fe$_T$ extractions were performed on ashed samples (8 h at 550°C) using HNO$_3$–HF–H$_3$BO$_3$–HClO$_4$. All Fe concentrations were measured via atomic absorption spectrometry and replicate extractions gave a relative standard deviation of <4% for all steps, leading to <8% for calculated Fe$_{\text{HR}}$ (see Supplementary Information for full discussion of data quality). Fe$_{\text{Py}}$ was calculated from the wt% of sulphide extracted as Ag$_2$S using hot Cr(II)Cl$_2$ distillation$^{58}$. A boiling HCl distillation before the Cr(II)Cl$_2$ distillation ruled out the potential presence of acid volatile sulfides in our samples. Pyrite extractions give reproducibility for Fe$_{\text{Py}}$ of 0.005 wt%, confirming high precision for this method. Analysis of a certified reference material (PACS-2, Fe$_T$ = 4.09 ± 0.07 wt%, $n$ = 4; certified value = 4.09 ± 0.06 wt%) confirms that our method is accurate. Replicate analyses ($n$ = 6) gave a precision of ± 0.06 wt% for Fe$_T$, and a relative standard deviation of <5% for the Fe$_{\text{HR}}$/Fe$_T$ ratio.
Calibration in modern and ancient marine environments suggests that $\text{Fe}_{\text{HR}}/\text{Fe}_T < 0.22$ indicates deposition under oxic water column conditions, while $\text{Fe}_{\text{HR}}/\text{Fe}_T > 0.38$ indicates anoxic conditions$^1$. Ratios between 0.22–0.38 are considered equivocal, and may represent either oxic or anoxic depositional conditions. For sediments identified as anoxic, $\text{Fe}_\text{py}/\text{Fe}_{\text{HR}} > 0.8$ is diagnostic for euxinic conditions and $\text{Fe}_\text{py}/\text{Fe}_{\text{HR}} < 0.7$ defines ferruginous deposition$^1$. This also applies to carbonate-rich sediments that have not undergone late stage dolomitisation$^{28}$, on the condition that $\text{Fe}_T > 0.5\text{wt}\%$. Where $\text{Fe}_T$ is very low (<0.5wt%), this may indicate deposition under oxic conditions$^{28}$. However, wherever possible we consider together data obtained from siliciclastic horizons interbedded with and/or associated with carbonate rocks contained within the same m- to dm-scale depositional cycle. Fe-speciation in carbonate and siliciclastic rocks gives consistent signals in the Nama Group (Figure 2), supporting the application of this proxy in carbonate rocks$^5,^{28}$.