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Nickel and zinc micronutrient availability in Phanerozoic oceans

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Abstract
Nickel and zinc are both bio-essential micronutrients with a nutrient-like distribution in the modern ocean, but show key differences in their biological functions and geochemical behavior. Eukaryotic phytoplankton, and especially diatoms, have high Zn quotas, whereas cyanobacteria generally require relatively more Ni. Secular changes in the relative availability of these micronutrients may, therefore, have affected the evolution and diversification of phytoplankton. In this study, we use a large compilation of Ni and Zn concentration data for Phanerozoic sediments to evaluate long-term changes in Ni and Zn availability and possible links to phytoplankton evolution. Modern data suggest that organic-rich sediments capture the dissolved deep ocean Ni/Zn ratio, regardless of local depositional conditions. We use this observation to constrain Ni/Zn ratios for past oceans, based on data from the sedimentary record. This record highlights long-term changes in the relative availability of these micronutrients that can be linked to the (bio)geochemical conditions on the Earth's surface. Early Palaeozoic oceans were likely relatively Ni rich, with sedimentary Ni/Zn ratios for this interval mostly being around ~1 or higher. A comparison with Phanerozoic strontium-, carbon-, and sulfur-isotopic records suggests that the late Palaeozoic decrease in sulfidic conditions and increase in hydrothermal inputs and organic-carbon burial rates caused a shift towards more Zn-rich conditions. Mesozoic and Cenozoic sediments show relatively Zn-rich oceans for these time intervals, with sedimentary Ni/Zn ratios mostly being around ~1 or lower. These observations imply that the diversification of the dominant groups of modern eukaryotic phytoplankton occurred in relatively Zn-rich oceans and that these organisms still carry this signature in their stoichiometries. However, the Phanerozoic transition to a more Zn-rich ocean pre-dates the origin and diversification of modern eukaryotes and, therefore, this transition was likely not the main direct cause for eukaryotic diversification in the Mesozoic and Cenozoic Eras.

1 INTRODUCTION

Many trace elements are essential to life, and their availability in the ocean exerts control on phytoplankton productivity and the cycling of major nutrients (e.g., Morel et al., 1991, 2014). Like major nutrients, these trace elements are often depleted in the modern surface ocean (e.g., Bruland, 1980; Schlitzer et al., 2018), suggesting that some trace elements may be co-limiting and that phytoplankton have evolved to efficiently utilize them (Moore et al., 2013; Morel, 2008 and references therein). Different groups of phytoplankton, however, have different elemental requirements, with a particularly strong contrast between prokaryotes and eukaryotes (e.g., Twining...
These differences have been suggested to reflect the evolutionary history of phytoplankton groups, with modern phytoplankton stoichiometries reflecting the conditions in which the organisms evolved (Da Silva & Williams, 2001; Morel, 2008; Quigg et al., 2003). Trace-element concentrations in the ocean have indeed undergone major changes throughout Earth history, mostly as a result of changing ocean redox conditions and weathering patterns (e.g., Anbar & Knoll, 2002; Large et al., 2015; Robbins et al., 2016). Prokaryotes dominated the Archean and Proterozoic oceans and cyanobacteria show metal requirements that are consistent with their evolution in the ferruginous and sulfidic environments that were prevalent at those times (Saito et al., 2003). These primary producers show a preference for elements like Co, Fe, and Ni that would have been relatively more soluble in the reducing oceans of the early Earth compared to an element like Zn, that has a strong affinity for sulfides and is more abundant in eukaryotic phytoplankton (Morel et al., 1994; Saito et al., 2002, 2003; Sunda & Huntsman, 1995; Twining & Barnes, 2013). To some degree, the diversification and evolution of metal-binding proteins likely also reflect these changes in ocean chemistry, so that metal availability may even be a limiting factor in phytoplankton evolution (Dupont et al., 2006; Dupont, Butcher, et al., 2010).

Conversely, however, phytoplankton also control trace-element availability and distribution patterns in the ocean on different temporal and spatial scales (e.g., Sunda, 2012). On longer timescales, biological uptake and subsequent burial of trace elements affects removal from the dissolved pool and thereby their availability in the global ocean (e.g., Algeo & Maynard, 2004). Indirectly, phytoplankton also control ocean trace-element concentrations and distributions through their impact on ocean redox conditions. Oxygenic photosynthesis and the burial of reduced organic carbon have contributed to the stepwise oxygenation of the ocean and atmosphere since the Archean, which was associated with major changes to ocean trace-element budgets due to the variable solubility of different elements under different redox conditions (e.g., Anbar & Knoll, 2002; Saito et al., 2003; Scott et al., 2008).

This two-way interaction between trace-element availability and phytoplankton complicates the assessment of any causal relationships between their co-evolution over geological timescales. For the case of Zn, some proxy records suggest relatively constant Zn availability over Earth history (Robbins et al., 2013; Scott et al., 2013), implying that biological innovation rather than metal availability would have controlled phytoplankton evolution (see review in Robbins et al., 2016). Assessing the causal relationship between the chemical and biological evolution of the ocean is further complicated by the observation that phytoplankton often have the ability to replace a poorly available element with one that is more readily available (e.g., Morel, 2008; Price & Morel, 1990; Sunda & Huntsman, 1995). While the exact causal relationships remain up for debate, the link between the evolution of the marine biosphere and elemental concentrations in the ocean is well established (Anbar & Knoll, 2002; Da Silva & Williams, 2001; Dupont, Butcher, et al., 2010; Large et al., 2015; Morel, 2008; Quigg et al., 2003; Robbins et al., 2016; Saito et al., 2003; Williams & Da Silva, 2003; Zerkle et al., 2005).

Here we focus on these questions for the Phanerozoic Eon. On the modern Earth, phytoplankton account for over 45% of annual net primary production (Field et al., 1998). While cyanobacteria numerically dominate modern phytoplankton, eukaryotes dominate organic matter export flux (Falkowski et al., 2004). The dominant groups of modern eukaryotic phytoplankton, however, did not evolve until the Mesozoic and diatoms in particular continued to diversify well into the Cenozoic (e.g., Armbrust, 2009; Benoist et al., 2017; Falkowski et al., 2004). Nutrient availability is considered to also play a major role in origination rates of marine organisms during the Phanerozoic Eon (Cárdenas & Harries, 2010). The role of micronutrient availability in controlling the varying dominance of different phytoplankton groups during the Phanerozoic, however, remains relatively poorly understood, even though modern groups of phytoplankton likely have different micronutrient requirements to dominant Palaeozoic or Proterozoic groups. A recent comparative genomic analysis suggests that a switch to lower metal availability in the Mesozoic Era may have contributed to a key transition in phytoplankton communities around this time (Zhang et al., 2022).

Proxy records of micronutrient availability are relatively scarce, but can provide valuable information in addition to the inferences from culturing, modelling, genomic, and modern ocean studies discussed above. Trace-element concentrations of sedimentary pyrite suggest there may have been cyclic alterations in Phanerozoic trace-element availability that can be linked to evolutionary and extinction events, but do not reveal a major long-term shift that can directly be linked to the transition to modern eukaryotes (Large et al., 2015). Other proxy records have also revealed significant long-term changes in the availability of micronutrients, but mostly focus on the longer-term transition from Archean to Phanerozoic (Isson et al., 2018; Robbins et al., 2013, 2016; Scott et al., 2013). These studies highlight the relevance of proxy records in assessing the link between phytoplankton evolution and environmentally driven changes in trace-element concentrations, but do not directly evaluate the role of micronutrient availability in relation to Phanerozoic phytoplankton diversification. In this study, we, therefore, focus on the Phanerozoic availability of two trace elements with distinctly different biological functions and requirements in modern eukaryotes versus cyanobacteria: Ni and Zn.

Nickel and zinc are both essential micronutrients with similar geochemical behavior. The elements both show a nutrient-like distribution in the modern ocean with low concentrations in the surface due to uptake by marine primary producers. However, these two elements also exhibit fundamental differences in their biological roles, cell quotas in different groups of phytoplankton, and geochemical behavior. In general, eukaryotic phytoplankton are known to have high Zn quotas, whereas cyanobacteria use relatively more Ni (Twining & Baines, 2013). We present a data compilation of Ni and Zn concentrations from Phanerozoic organic-rich sediments. By comparison to an extensive modern dataset we suggest that Ni/Zn ratios of organic-rich sediments can be used to constrain the relative...
availability of these elements in past oceans. Phanerozoic Ni/Zn data show major changes in the relative abundance of these micronutrients, particularly around the Late Palaeozoic and Early Mesozoic. We evaluate the possible links to the evolution of the marine biosphere and geochemical conditions on the Earth's surface.

2 | BACKGROUND INFORMATION

2.1 | Nickel and Zn as micronutrients

Nickel is a bio-essential trace element with a function in a number of critical enzymes relevant to the global biological cycling of carbon, nitrogen, and oxygen (review in Ragsdale, 2009). Nickel, for example, forms the center of urease, which catalyzes the hydrolysis of urea. As a result, the Ni content of cultured phytoplankton is generally low, but increases dramatically when organisms are grown on urea (Price & Morel, 1991). Nickel limitation of marine Synechococcus has been linked to the Ni-specific form of superoxide dismutase (SOD), which protects the cells from oxidative stress by catalyzing the breakdown of superoxide (Dupont et al., 2008). In culture, the element has also been shown to be bio-limiting to the diazotrophic cyanobacteria Trichodesmium, responsible for nearly half of the nitrogen fixation in the modern oceans globally (Bergman et al., 2013; Ho, 2013). Anaerobic microbes use Ni as part of the NiFe hydrogenase and CO dehydrogenase enzymes that catalyze the reversible oxidation of H2 and CO, respectively (Ragsdale, 2009). The Ni-containing methyl-coenzyme M reductase (MCR) is a key enzyme for methanogenesis and the anaerobic oxidation of methane (Scheller et al., 2010). This reliance of methanogens on Ni availability has been suggested to impact methane production on the early earth, when Ni availability might have been more variable (Konhauser et al., 2009). In short, many of these Ni enzymes are particularly important for cyanobacteria and in anaerobic conditions.

By contrast, the biological function of Zn is mostly important for eukaryotes, while Zn requirements of cyanobacteria are relatively low (e.g., Twining & Baines, 2013). Zinc is utilized in many different Zn-specific enzymes, with a particular significance in the ocean as a cofactor in the carbonic anhydrase and alkaline phosphatase enzymes. Zinc also has an important function in RNA polymerase and a central role in DNA duplication (Coleman, 1998). Carbonic anhydrase regulates the equilibrium between different inorganic-carbon sources, and thereby catalyzes a number of important processes, including the photosynthetic assimilation of organic carbon, the release of CO2 during respiration, and the mineralization of calcium carbonate. Alkaline phosphatase allows the recycling of organic phosphate when the inorganic form is scarce. Marine eukaryotes are important alkaline phosphatase producers and show relatively high Zn uptakes, whereas culture studies have shown that Zn can be co-limiting for several groups of eukaryotic algae (e.g., Shaked et al., 2006). Low Zn availability, for example, limits growth rates and is the second most limiting metal nutrient after Fe for the dinoflagellate Symbiodinium kawagutii (Rodriguez & Ho, 2018). Diatoms are known to have particularly high Zn requirements, based on bulk particulate data and culture studies (e.g., Anderson et al., 1978; Morel et al., 1994; Twining & Baines, 2013). More generally, larger cells have also been found to contain more Zn, whereas Ni stoichiometries are negatively related to cell volume (Twining et al., 2004). To summarize, Zn is a key micronutrient, with particularly high demands by modern eukaryotic phytoplankton.

2.2 | Nickel and Zn in the modern ocean

Differences in the biological function and geochemical behavior of Ni and Zn are also apparent from their distribution in the modern ocean. In general, the elements follow a nutrient-like distribution, with low concentrations in the surface as a result of uptake by primary producers and higher concentrations at depth. However, there are notable differences between the elements. Firstly, unlike Zn and most other bio-active trace elements, Ni concentrations in the surface ocean do not reach values below about 1.8 nmol/kg (e.g., Bruland, 1980; Middag et al., 2020). It has been suggested that this feature is the result of a biologically unavailable Ni pool (Dupont, Buck, et al., 2010; Mackey et al., 2002), but it may also reflect the slow kinetics of uptake caused by the inertness of the Ni3+ ion (Morel et al., 2014). The other main difference is the behavior of the elements at high latitudes, which is particularly well established in the Southern Ocean (e.g., Archer et al., 2020; Janssen et al., 2020; Lösch, 1999; Middag et al., 2020; Figure S1). Enhanced uptake of Zn by diatoms in the Southern Ocean leads to relatively high Zn concentrations in deeper Southern Ocean waters following remineralization. Dissolved Ni isotope and concentration data points to a strong contrast across the Polar Front of the Southern Ocean. South of the Polar Front, Ni uptake is relatively low as diatoms dominate primary production, whereas higher uptake of Ni North of the Polar front is most consistent with cyanobacteria as a dominant control on Ni uptake (Archer et al., 2020). These observations are generally consistent with our current understanding of Ni and Zn uptake and requirements from culture studies, with relatively higher Ni requirements in areas dominated by prokaryotes.

Dissolved Ni and Zn concentrations in the Black Sea highlight redox controls on the distribution and availability of these elements (Landing & Lewis, 1991; Tankéré et al., 2001). Low concentrations of Zn in the highly sulfidic waters of the deep Black Sea suggest that Zn forms insoluble complexes with sulfide that cause a strong drawdown of Zn to the sediments. By contrast, Ni concentrations remain relatively high in the deep Black Sea despite the high sulfide content. These observations are consistent with predictions from equilibrium thermodynamics that suggest that Zn-sulfide species are considerably more stable than Ni-sulfide complexes (Al-Farawati & van den Berg, 1999). In contrast to Zn, Ni is incorporated into pyrite (Huerta-Díaz & Morse, 1992). Strong Ni concentration and isotope gradients around the Black Sea chemocline highlight the element’s affinity for Mn-oxides (Tankéré et al., 2001; Vance et al., 2016), as also stressed in recent
studies on sedimentary Ni-cycling (Gueguen & Rouxel, 2021; Little et al., 2020). Nickel concentrations in sediments from highly productive continental-margin upwelling systems and ancient shales have been shown to correlate strongly with the total organic-carbon content (Algeo & Maynard, 2004; Böning et al., 2015; Ciscato et al., 2018; Tribovillard, 2021).

2.3 | Eukaryotic phytoplankton evolution

The earliest definitive evidence for eukaryotes points to an origin 1.7–1.6 billion years ago, with further diversification and increased production in the Neoproterozoic (Butterfield, 2015; Knoll et al., 2006). Early Palaeozoic phytoplankton fossils are dominated by acritarchs, a nondistinct group of likely eukaryotic organic-walled microfossils, but acritarch diversity decreased substantially around the Devonian/Carboniferous boundary (~359 Ma, Katz et al., 2007 and references therein). The three phytoplankton groups that dominate the modern ocean (coccolithophores, diatoms, and dinoflagellates) did not rise to ecological prominence until the Mesozoic Era (251–65 million years ago), after the Permian–Triassic extinction event (Falkowski et al., 2004). This shift in dominant groups of phytoplankton from the Early Palaeozoic to the Mesozoic Era is separated by an interval of relatively low phytoplankton diversity during the Carboniferous, Permian, and Early Triassic, referred to by some authors as the “Phytoplankton Blackout” (Riegel, 2008). However, this observation may instead reflect an absence of cysts in the fossil record, as the presence and abundance of planktotrophic larvae of marine invertebrate organisms and filter and suspension feeding organisms suggest sufficient primary production (Servais et al., 2016). Finally, diatom diversity only recently increased to modern levels, through two major pulses at the Eocene/Oligocene boundary and in the middle and late Miocene (Armarust, 2009; Benoist et al., 2017; Falkowski et al., 2004). Diatoms are thought to be the major contributors to primary productivity and carbon export among all photosynthetic organisms in the modern ocean, largely due to their abundance in highly productive regions (Benoist et al., 2017; Field et al., 1998).

Many different processes may have impacted the origin and further diversification of the groups of phytoplankton that dominate the modern ocean (Katz et al., 2007). These include changes in biological innovation, land plant evolution, orogeny, volcanism, ocean redox state, plankton stoichiometry, climate, mass extinctions, and sea level. Many of these processes are ultimately linked to phytoplankton diversification through their impact on the availability of nutrients (Martin & Quigg, 2012; Sharoni & Halevy, 2022). A change in nutrient availability has also been proposed to explain the apparent demise of acritarchs in the Late Palaeozoic. Encystment might have been common in the middle Palaeozoic due to low-nutrient levels, whereas phytoplankton may not have needed encystment due to elevated nutrient levels in the Carboniferous to Permian periods (Servais et al., 2016).

In summary, we can roughly distinguish four main Phanerozoic intervals based on phytoplankton diversity: (1) the early to middle Palaeozoic, with a dominance of acritarchs in likely low-nutrient conditions; (2) the late Palaeozoic to early Mesozoic “Phytoplankton Blackout,” with low phytoplankton diversity in the fossil record, but possibly due to a lack of cyst formation in higher nutrient conditions; (3) the Mesozoic–Cenozoic, with the arrival and diversification of the modern groups of phytoplankton following the Permian–Triassic extinction event; (4) the modern ocean, where diatoms dominate primary production since the mid-Cenozoic.

3 | DATA

We have compiled a large amount of sedimentary elemental concentration data from publicly available literature sources and contribute new data from various time intervals. This compilation is published together with this paper in the Appendix S1–S4, where Appendix S1 hosts all compiled modern elemental concentration data, Appendix S2 all paleo data, and Appendix S3 a combined file with all data in one sheet. Two major sources of literature data are the PANGAEA database, hosted by the Alfred Wegener Institute, Helmholtz Center for Polar and Marine Research (AWI) and the Center for Marine Environmental Sciences, University of Bremen (MARUM) and a recent publication by Algeo and Liu (2020). In addition, we present previously unpublished data from several time intervals and locations (see Appendix S1–S4).

3.1 | Sample bias and data availability

The compilation approach used here has an inherent bias. Trace elements are generally enriched in organic-rich sediments and used as redox proxies. A compilation of publicly available trace-element data will, therefore, be biased towards time intervals and conditions that favored the deposition of organic-rich sediment deposition. These data, therefore, may not necessarily reflect global ocean conditions over longer timescales. For example, widespread organic-rich sediment deposition occurred in the Mesozoic Era during so-called Oceanic Anoxic Events (OAEs, e.g., Jenkyns, 2010), and the dataset includes a lot of data for the Cenomanian–Turonian OAE 2 interval, when organic-rich sediment deposition occurred on a global scale. These events were relatively short-lived (103–104 years) compared to the duration of the Mesozoic Era, represent major environmental perturbations to background conditions during this time interval, and have been associated with the global drawdown of dissolved trace-element micronutrient inventories (e.g., Owens et al., 2016). Trace-element data from these intervals, therefore, do not necessarily represent conditions during the wider Mesozoic Era. However, the size of the dataset generally ensures that considerable amounts of data are included for pre- and post-event intervals. Changes in the Ni and Zn data over these events are relatively small compared to observed secular changes (see Figure S2). Additionally, there is a geographic bias for some intervals. The sample sets for the Devonian and Carboniferous Eras are biased towards data from the North...
American continent, simply because much more data have been generated there (e.g., Algeo & Liu, 2020 and references therein). The influence of possible geographic biases will be evaluated by comparison of modern environments in the next section. Despite these possible caveats, the size of the dataset is substantial and can still provide relevant information on secular changes in Ni and Zn availability.

4 | NI/ZN RATIOS OF MODERN MARINE SEDIMENTS

Compiled Ni/Zn ratios of modern marine organic-rich sediments are very similar to deep ocean-dissolved compositions and vary around ~1 (Figure 1a,b). This similarity applies to different marine settings, from open-ocean continental-margin settings to hydrographically restricted basins, and the variance in Ni/Zn ratios decreases with increasing total organic-carbon (TOC) concentrations (Figure 2). The similarities between different settings are remarkable, as processes and trace-element cycling in different environments are fundamentally different and lead to different levels of sedimentary enrichments for other transition metals (e.g., Sweere et al., 2016). For Ni and Zn specifically, dissolved Ni and Zn concentrations in the Black Sea highlight the different geochemical behavior of these elements. Dissolved Zn concentrations in the deep Black Sea are low due to sulfide formation, in contrast to Ni for which the dissolved concentrations remain relatively high at depth (Landing & Lewis, 1991). Apparently, the higher affinity of Zn for sulfides does not lead to a higher relative enrichment of Zn over Ni in Black Sea sediments, compared to other regions or the dissolved concentrations of these elements in the global ocean. This apparent discrepancy can be explained if the Black Sea is in steady state with regards to Ni and Zn and if Ni/Zn ratios of net inputs to the basin approach the mean global deep ocean composition. One explanation for slightly elevated Ni/Zn ratios of Black Sea sediments compared to the global deep ocean ratio could be higher Ni/Zn values of
FIGURE 2 Nickel and Zn concentrations in modern marine organic-rich sediments from different locations. The grey shading reflects the range in dissolved deep ocean concentrations as indicated in Figure 1. The large majority of sediment data fall within this range, especially for highly organic-rich sediments with TOC concentrations of >10%. A group of Black Sea samples deviate from the dominant pattern with relatively high Ni concentrations. These samples are predominantly from two stations taken at intermediate water depths (380 and 600 m), just below the chemocline and, therefore, do not directly represent deposition in the highly euxinic deep Black Sea.

FIGURE 3 Nickel and zinc concentrations of Phanerozoic sediments and diversification of eukaryotes. (a) Phanerozoic Ni/Zn ratios of organic-rich (TOC > 2%) sediments. Grey bands indicate the modern deep ocean composition (Figure 1a). (b) Violin plots with samples grouped per time interval. Sample counts indicated at the top. Right of the panel, Ni/Zn ranges are indicated for diatoms (Monterey Bay and Southern Ocean) and Trichodesmium (North Atlantic Ocean, 25th to 75th quartile) for comparison, taken from compilation by Twining and Baines (2013). (c) Diversification of eukaryotic phytoplankton. The grey trends show the relative change in diversity of the different groups, taken from Katz et al. (2007), the dashed line goes back to earliest possible origins (Benoiston et al., 2017).
intermediate water depths, suggesting that the relatively high Ni found in those sediments may also be related to redox-driven Mn-cycling (Figure 2; Vance et al., 2016). Additionally, Mn cycling may aid transport of Ni to depths, similar to the particulate shuttle that has been suggested to affect other trace elements (e.g., Algeo & Tribovillard, 2009; Dellwig et al., 2010), resulting in relatively high sedimentary concentrations without strong drawdown as sulfides. Regardless of the detailed processes and their controls, the Ni/Zn ratio of different modern organic-rich (TOC > 2%) sediments consistently reflect the observed range in the dissolved deep ocean composition. This similarity between organic-rich sediments and the deep-ocean composition implies that organic-rich marine sediments from the sedimentary record can provide an estimate of Ni and Zn availability in past oceans. For the rest of the discussion, we use this observation to reconstruct the dissolved Ni/Zn ratio of Phanerozoic oceans from Ni and Zn concentrations in the sedimentary record.

4.1 | Ni/Zn ratios of Phanerozoic sediments

Ni/Zn ratios of Phanerozoic sediments show a broad range that varies roughly around the crustal composition (Figure 1c). Absolute Ni and Zn concentrations, however, are generally above crustal concentrations: 89% and 86% of all samples with TOC > 2% are enriched in Ni and Zn compared to crustal values, respectively; 57% of samples are at least 50% enriched in both elements relative to upper crustal compositions (Figure S3). A dominance of detrital minerals in these sediments, therefore, cannot directly explain the similarity between crustal and organic-rich Phanerozoic sediment Ni/Zn ratios. Instead, this similarity implies that, on long timescales, Ni and Zn inputs largely derive from the crust and the elements have similar solubilities in Phanerozoic oceans. The range in Ni/Zn ratios is not distributed equally over the Phanerozoic (Figure 1d); the different intervals of Phanerozoic phytoplankton diversity, identified in the introduction, show different Ni/Zn ratios. Low Ni/Zn values (<0.1) are almost exclusively found for sediments of mid-Palaeozoic age or younger, whereas high Ni/Zn values are largely limited to Palaeozoic sediments.

Ni/Zn ratios of Phanerozoic organic-rich sediments show clear temporal patterns (Figure 3). Highest values are observed for the early Palaeozoic Era, followed by minima in the Late Carboniferous and Permian Periods and relatively low values during much of the Mesozoic and Cenozoic Eras. Filtering for different TOC values does not affect the dominant patterns observed, suggesting that, as for the modern ocean, the Ni/Zn ratios of organic-rich sediments likely reflect the Ni/Zn of the deep ocean during deposition (Figure S4). We do not observe a similar cyclicity in our data as found by Large et al. (2015), who studied the Phanerozoic trace-element concentrations of pyrite. However, the focus of that study is on absolute variations between nutrient-rich and -poor conditions, rather than changes in the relative availability of the different elements that we evaluate here. In both datasets, intervals in the Carboniferous and Permian stand out as being particularly trace-element rich.

4.2 | Controls on Phanerozoic seawater Ni/Zn values

In steady state conditions, the dissolved concentration of any element in the ocean can be described by:

\[
C_{\text{ocean}} = r_{\text{res}} \left( \frac{F_{\text{in}}}{M_{\text{water}}} \right)
\]  

where \(C_{\text{ocean}}\) is the concentration of an element in the ocean, \(F_{\text{in}}\) is the total input flux, \(r_{\text{res}}\) is the residence time of the element in the ocean, and \(M_{\text{water}}\) is the total mass of ocean water. Following from this, we can describe the dissolved Ni/Zn ratio of the ocean as:

\[
\frac{[\text{Ni}]}{[\text{Zn}]}_{\text{ocean}} = \frac{r_{\text{res Ni}}}{r_{\text{res Zn}}} \times \frac{F_{\text{in Ni}}}{F_{\text{in Zn}}}
\]

or expressed as log-ratios:

\[
\log[\text{Ni/Zn}]_{\text{ocean}} = \log \left( \frac{r_{\text{res Ni}}}{r_{\text{res Zn}}} \right) + \log \left( \frac{F_{\text{in Ni}}}{F_{\text{in Zn}}} \right)
\]

In other words, in steady state conditions, the Ni/Zn ratio of the ocean is set by the relative proportion of inputs and residence times of these elements. Long-term changes in inputs or residence times may thus result in secular changes in the dissolved Ni/Zn of the ocean.

Inputs and residence times of Ni and Zn are still relatively poorly quantified for the modern ocean and the subject of ongoing research. Yet, as the \([\text{Ni}/\text{Zn}]_{\text{ocean}}\) ratio is well constrained for the modern ocean, we can use equation (3) to assess whether the current estimates of inputs and residence times for Ni and Zn are proportionally reasonable (Figure 4). For the modern ocean, Ni inputs are estimated at a combined total of \(5.1 \times 10^8\) mol yr\(^{-1}\) (or \(3.0 \times 10^{10}\) g yr\(^{-1}\)) leading to a residence time of \(21\) kyr (Little et al., 2020), whereas Zn inputs are estimated at a combined total of \(6.6 \times 10^8\) mol yr\(^{-1}\) (or \(4.32 \times 10^{10}\) g yr\(^{-1}\)) leading to an estimated residence time of \(21\) kyr (Little et al., 2014). The latter is consistent with the range in residence times (2.7–13.5 kyr) recently estimated based on Zn outputs (Dickson, 2022). Following equation 3 and using 11 kyr as the Zn residence time, this would put the \([\text{Ni/
Zn\textsubscript{ocean} at 1.48 mol/mol or 1.32 g/g and log[Ni/Zn]\textsubscript{ocean} at 0.17 (mol/mol) and 0.12 (g/g), which is well within the range observed in the modern deep ocean and just above the most commonly found values (Figure 2). This comparison suggests that, despite the large uncertainties that still come with estimates of global inputs and residence times of Ni and Zn individually, our current understanding of at least the relative residence times (\textit{t}_{\text{res Ni}}/\textit{t}_{\text{res Zn}}) and inputs (\textit{F}_{\text{in Ni}}/\textit{F}_{\text{in Zn}}) of Ni and Zn is reasonably good.

In the following discussion we evaluate our current knowledge of Ni and Zn inputs and residence times, and how potential variations over the Phanerozoic might explain the observed trends in Phanerozoic [Ni/Zn]\textsubscript{ocean}. We conclude that a transition to relatively more Zn-rich conditions occurred in response to lower sulfide burial, possibly aided by higher hydrothermal inputs and/or a change in the composition and/or rates of organic-carbon burial.

### 4.3 | Inputs

Generally, riverine inputs are considered dominant for both elements, but recently benthic and hydrothermal inputs (for Zn) have also been suggested to be relevant and larger than originally thought (Gueguen & Rouxel, 2021; Lemaître et al., 2020; Little et al., 2020; Roshan et al., 2016). The ratio (0.70 g/g) of Ni (47 ppm) to Zn (67 ppm) concentrations in the upper continental crust (Rudnick et al., 2003) is comparable to the ratio (0.55 g/g) of the estimated total riverine inputs (3.6 and 5.9 nmol/kg for Ni and Zn, respectively, Cameron & Vance, 2014; Little et al., 2014). Temporal variations in riverine input fluxes, therefore, are not expected to directly impact (\textit{F}_{\text{in Ni}}/\textit{F}_{\text{in Zn}}). One key difference between the two elements that may affect (\textit{F}_{\text{in Ni}}/\textit{F}_{\text{in Zn}}) over time is the hydrothermal input of these elements, or potentially other forms of basalt-seawater interaction.
interaction. Evidence emerging from the GEOTRACES project has highlighted hydrothermal input of Zn as a possibly significant source to the modern ocean (Roshan et al., 2016). By contrast, there is no direct evidence for a significant hydrothermal input of Ni and hydrothermal sites may instead be a net sink of Ni through scavenging (Ciscato et al., 2018 and references therein). Recent studies suggest that a benthic flux is likely significant for both elements (Gueguen & Rouxel, 2021; Lemaitre et al., 2020; Little et al., 2020), though it is currently not well quantified. However, any long-term variations in this flux are probably strongly affected by the global redox conditions that also affect residence times, discussed below. We, therefore, conclude that a long-term temporal increase in the relative proportion of global hydrothermal input may lead to a relatively higher Zn input and availability in the ocean, compared to Ni. Based on our current knowledge, other changes to inputs are not expected to affect the ocean's Ni/Zn ratio much.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio can be used as a tracer for the balance between mid-ocean ridge volcanism ($^{87}\text{Sr}/^{86}\text{Sr} = 0.703$) and riverine ($^{87}\text{Sr}/^{86}\text{Sr} = 0.711$) inputs (e.g., McArthur et al., 2020 and references therein). Marine carbonates capture the $^{87}\text{Sr}/^{86}\text{Sr}$ compositions of past oceans and thereby provide a long-term record of relative importance of these inputs, with high $^{87}\text{Sr}/^{86}\text{Sr}$ values being indicative of relatively higher riverine inputs. General patterns in $^{87}\text{Sr}/^{86}\text{Sr}$ and Ni/Zn are comparable, and minima in $^{87}\text{Sr}/^{86}\text{Sr}$ during the Permian and mid-Jurassic correspond to relatively low Ni/Zn (Figure 5). Higher Zn input from hydrothermal systems or other forms of basalt-seawater interaction may, therefore, partly explain the lower Ni/Zn ratios during these intervals. Conversely, the Cenozoic increase in $^{87}\text{Sr}/^{86}\text{Sr}$, and inferred decrease in relative hydrothermal inputs, may explain a rise in Ni/Zn towards modern values of −1 towards the end of the Cenozoic. Sedimentary Cenozoic Ni/Zn data, however, are scarce and the evolution of Cenozoic Ni/Zn seawater can, therefore, not be constrained in detail.

### 4.4 Residence times

Ocean redox conditions are likely the dominant control on differences between Ni and Zn residence times over Phanerozoic timescales, mostly because of the strong affinity of Zn for sulfides compared to Ni. In an ocean where sulfidic conditions are relatively common, the dissolved Ni/Zn ratio is likely relatively high due to the burial of Zn-sulfides. Geochemical models have suggested that this leads to relatively high Ni/Zn ratios in Archean and Proterozoic oceans (Saito et al., 2003). It is also illustrated by dissolved data from the Black Sea, where Ni/Zn ratios in deep waters are much higher than values in the open ocean; the mean dissolved Black Sea Ni/Zn ratio for samples below the chemocline (>200 m depth) is $30 \pm 6$ (g/g, 1 SD, $n = 13$) with log(Ni/Zn)$_{\text{deep Black Sea}}$ at 1.5 (Vance et al., 2016), which is comparable to the highest values found in the Phanerozoic sediment compilation (Figure 4).

**FIGURE 5** Phanerozoic Ni/Zn ratios compared to strontium-, carbon-, and sulfur-isotope records. Data compiled in Prokoph et al. (2008), figure modified from Hannisdal and Peters (2011). Grey bands indicate the modern deep ocean composition (Figure 1a).

Estimates of modern ocean output fluxes associated with Fe- or Mn-oxide burial are similar for Ni and Zn (Gueguen & Rouxel, 2021; Little et al., 2014, 2020). Variations in these oxic outputs over time may, therefore, not necessarily be expected to impact these尼/锌比值。
estimates, however, come with considerable uncertainty and the Ni and Zn sinks associated with Fe- or Mn-oxide burial are a topic of ongoing and recent research. The available dissolved Black Sea data suggest that the Mn-oxide burial sink may be more relevant for Ni, as chemocline samples show high Ni concentrations likely associated with the reductive dissolution of Mn-oxides (Tankéré et al., 2001; Vance et al., 2016). If there is a difference between the elements, outputs associated with Fe- or Mn-oxide burial potentially affect Ni more than Zn. Organic-carbon burial may impact the residence times of these elements, the extent of which likely depends on the composition of the organic material buried, as material predominantly derived from eukaryotes probably has lower Ni/Zn ratios. Considering the strong correlation of Ni to TOC in modern (Böning et al., 2015; Ciscato et al., 2018) and ancient (Algeo & Maynard, 2004; Tribovillard, 2021; Figure S4) sediments it is possible that the amount of organic-carbon burial impacts the Ni residence time more than it does Zn, with higher organic-carbon burial corresponding to lower $\frac{\text{Ni}}{\text{Zn}}$. To summarize, high dissolved Ni/Zn ratios are expected in oceans with a relatively large sulfide sink, that is, in more reducing oceans, whereas low Ni/Zn ratios may occur in oceans with relatively high organic-carbon and/or Mn-oxide burial, depending on the composition of the organic matter buried. Phanerozoic sulfur-isotope records of marine carbonates are thought to reflect the isotopic composition of ambient seawater, which can provide information on the relative proportion of sulfide vs sulfate burial (e.g., Kampschulte & Strauss, 2004). A compilation record shows a long-term decrease in the Palaeozoic Era, with a minimum in the Late Carboniferous and Permian Periods, reflecting low sulfide burial that corresponds to minima in Ni/Zn (Figure 5; Prokop et al., 2008). This correlation suggests that a lowering of the sulfide burial flux towards the end of the Palaeozoic contributed to a relatively higher Zn availability. The same time interval features maxima in $\delta^{13}C$ that indicate that the proportion of organic-carbon burial was relatively high, which is remarkable as carbon and sulfide burial generally covary. This apparent discrepancy suggests a large proportion of organic-carbon burial occurred in low-S environments (e.g., Berner & Raiswell, 1983). We conclude that low sulfide burial increased Zn residence times and, possibly aided by higher Ni burial with low-S organic carbon, caused a decrease in dissolved Ni/Zn ratio or, in other words, an increase in the relative Zn availability.

4.5 | The co-evolution of phytoplankton and Ni and Zn cycles in Phanerozoic oceans

Variation in the relative availability of dissolved Ni and Zn in the Phanerozoic coincides with temporal changes in the evolution and diversification of key groups of phytoplankton (Figure 3). The acritarch-dominated Early Palaeozoic ocean is considered to have been relatively nutrient poor (Servais et al., 2016) and shows consistently high (~1) Ni/Zn values, suggesting relatively low Zn availability. The lack of fossil remnants of Late Palaeozoic phytoplankton groups makes it difficult to assess the links between phytoplankton and micronutrient availability, but the suggestion that the Carboniferous and Permian might have been relatively nutrient-rich (Large et al., 2015; Servais et al., 2016) would be supported by the Ni/Zn patterns presented here; the lowest Ni/Zn ratios and highest absolute Ni and Zn concentrations are found during that time interval (Figure S6). From the early Mesozoic Era, red eukaryotic phytoplankton began to displace green eukaryotic algae in the ocean (e.g., Falkowski et al., 2004; Katz et al., 2007). While the exact timing of this rise to dominance is difficult to constrain, dinoflagellates and coccolithophores likely emerged in the Triassic, whereas evidence for the first diatoms points to emergence later in the Mesozoic. The Mesozoic and Cenozoic Eras are generally characterized by low (<1) Ni/Zn ratios, that is, relatively high Zn availability. Although the causal links are difficult to prove, it is possible that the high Zn availability of Mesozoic and Cenozoic oceans promoted development of modern types of eukaryotic phytoplankton, by favoring the evolution of Zn enzymes that provided a competitive advantage. Conversely, it is possible that the rise to dominance of the modern phytoplankton groups also impacted $\frac{\text{Ni}}{\text{Zn}}$ and thereby the relative concentrations of Ni and Zn in the ocean. Modern ocean Ni/Zn concentrations are generally higher than those found for most of the Mesozoic and Cenozoic. Thus, the rise and diversification of diatoms in the Cenozoic might have lowered the residence time of Zn in the ocean and brought the Ni/Zn ratio of seawater back to values of about 1.

Based on the data presented here, it appears that the Phanerozoic transition to a more Zn-rich ocean predates the origin and diversification of modern eukaryotes and was driven by changes in the geochemical conditions on the Earth’s surface. As such, a shift in micronutrient regimes and transition to more Zn-rich conditions does not appear to be the key driver of eukaryotic diversification from the Mesozoic Era. It is possible, though, that a shift in the relative availability of micronutrients may have provided a competitive advantage to organisms able to evolve biogeochemical functions/enzymes to use the more replete nutrients, when ecological space became available after the Permian–Triassic extinction event. In this view, evolving geochemical conditions on the Earth’s surface (ocean redox, ocean inputs), possibly forced by changes to the continental configuration (Pohl et al., 2022), would have set the nutrient conditions that affected phytoplankton evolution. These links certainly remain speculative, but the data presented here suggest that further investigation of micronutrient availability, as at least one aspect that contributed to the timing of eukaryotic development in the Phanerozoic, would be fruitful. Our findings also provide further support for the previously suggested links between phytoplankton evolution and ocean trace-element cycles (e.g., Morel, 2008; Robbins et al., 2016; Saito et al., 2003; Williams & Da Silva, 2003).

5 | CONCLUSION

Nickel and Zn concentrations of organic-rich Phanerozoic sediments highlight secular shifts in the relative availability of these...
micronutrients in past oceans. These changes occur at intervals of major (bio)geochemical change, including during shifts in weathering regimes and the sulfur and carbon cycles. Minima in Ni/Zn during the Late Carboniferous and Permian are found during intervals also associated with relatively high hydrothermal inputs (low $^{87}$Sr/$^{86}$Sr), low sulfide (low $\delta^{34}$S), and high organic-carbon (high $\delta^{13}$C) burial. This time interval also sees the transition from dominant Early Palaeozoic groups of phytoplankton, to modern types that started their diversification in the Early Mesozoic Era. The observations made here suggest that the modern groups of dominant phytoplankton developed in relatively Zn-rich oceans, also compared to the modern ocean, which appears to still be reflected in their stoichiometries. It is possible that the relatively Zn-rich conditions that have existed since the Late Palaeozoic and during the Mesozoic and Paleogene may have promoted the diversification of modern groups of eukaryotic phytoplankton following the Permian-Triassic extinction event. However, based on the compilation presented here, the transition to more Zn-rich conditions occurs well before the origin and diversification of modern eukaryotes. A change in micronutrient regimes, therefore, does not appear to be the primary and direct cause of modern eukaryotic development. These data, therefore, cannot provide a definitive assessment of the causal relationship between micronutrient availability and Phanerozoic phytoplankton evolution. Future research may use these observations to assess the causal mechanisms of these changes in more detail.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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1. Report


2. Supporting Information

**SUPPORTING INFORMATION**

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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