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Controls on nickel and zinc micronutrient availability in Phanerozoic oceans

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Dominant groups of modern eukaryotic phytoplankton did not evolve until the Mesozoic Era and likely have different micronutrient requirements to dominant Palaeozoic or Proterozoic groups. The role of micronutrient availability in controlling the varying dominance of different phytoplankton groups during the Phanerozoic, however, remains relatively poorly constrained due to a lack of proxy records. Here 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. 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.

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 may 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.