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Iron isotopes reveal iron cycling pathways during cyanobacterial blooms in boreal shield lakes

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Iron (Fe) plays a key role in regulating phytoplankton growth in ocean and freshwater systems. Since dissolved Fe (DFe) is constrained to low concentrations in surface waters, phytoplankton uptake can alter Fe cycling during periods of high productivity (blooms). However, several aspects of Fe uptake remain poorly understood. Here, we present a novel application of Fe isotopes combined with seasonal variations in concentrations and redox speciation of DFe and particulate Fe (PFe) during the progression of two cyanobacterial blooms in the oxic layers of a boreal shield lake (Lake 227) that has been the focus of a nutrient enrichment experiment for over 50 years. A large and diagnostic isotopic offset ($\Delta^{56}Fe_{dis\text{-}part}$ = +1.02 ± 0.40‰) between DFe and PFe, coupled with the prevalence of Fe(II) in PFe, was observed during the blooms, contrasting with the indistinguishable Fe isotope compositions of DFe ($\delta^{56}Fe_{dis}$) and PFe ($\delta^{56}Fe_{part}$) and the dominance of Fe(III) in PFe before and after the blooms. The preferential uptake of isotopically light dissolved Fe(II) by cyanobacteria is most likely the dominant process driving the observed changes in Fe cycling and $\delta^{56}Fe$ during the blooms. The prevalence of Fe(II) in PFe further suggests that Fe acquisition involves reductive Fe uptake and/or porin-mediated transport of photochemically produced Fe(II), highlighting the importance of Fe(II) bioavailability. Moreover, the presence of organic matter-rich, isotopically light particulate Fe ($\delta^{56}Fe_{part}$ = −0.7‰) in oxic waters during blooms may help explain the moderately negative $\delta^{56}Fe$ values preserved in some Precambrian sedimentary rocks. The difference in $\Delta^{56}Fe_{dis\text{-}part}$ between the first cyanobacterial bloom (+1.02 ± 0.40‰) and the second mixed cyanobacteria-chlorophyte bloom (+0.56 ± 0.04‰) suggests that distinct taxa-related Fe isotope fractionations are produced during growth. Fe isotopes serve as a diagnostic tool for investigating biogeochemical Fe processes during blooms and tracking Fe sources utilized by cyanobacteria and eukaryotic algae. This study highlights the importance of understanding Fe cycling and isotopic systematics during cyanobacterial blooms for improving bloom management and shows that primary productivity should be taken into account when interpreting $\delta^{56}Fe$ signatures in Precambrian sedimentary rocks.