

Constraining the elemental stoichiometry of early marine life

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ABSTRACT

The relative proportions of carbon, nitrogen, and phosphorus, commonly referred to as the Redfield ratio (106:16:1), have likely varied dramatically through Earth's history in response to changes in oceanic redox state and nutrient availability. However, there have been few attempts to track long-term secular patterns in the elemental stoichiometry of marine life. We use a sediment reactive-transport (diagenetic) modeling approach to provide new constraints on the elemental stoichiometry of marine ecosystems during Earth's early history, by simulating environmental conditions associated with the formation and deposition of suites of Archean sedimentary iron and phosphorus-bearing minerals. Our results suggest that siderite formation in porewaters linked to dissimilatory iron reduction but limited formation of authigenic P phases can only be reproduced when C to P ratios in marine biomass are at least 500 (mol/mol), approximately five times higher than the values that characterize the modern ocean. This constraint indicates that Archean oceans were strongly nutrient-limited.

INTRODUCTION

The ratio of carbon to nitrogen to phosphorus in modern marine biomass typically shows limited variation around the canonical Redfield ratio, which is 106(C):16(N):1(P) (Redfield, 1934). Observed variations in this elemental ratio can be explained in part by spatial heterogeneity in the chemical composition of seawater—more P-depleted regions and ecosystems typically have slightly higher C:P ratios (Weber and Deutsch, 2012; Sharoni and Halevy, 2022). Modern freshwaters also show considerable variation in elemental stoichiometries—more P-poor waters, which are dominated by single-celled cyanobacteria, are likewise associated with higher biomass C:P ratios (e.g., Crowe et al., 2008; Martiny et al., 2013). By extension, the C:P ratios of marine life during Earth's early history—when the oceans have been proposed to have had considerably lower dissolved P concentrations—may have been notably different (see Reinhard et al., 2017; Planavsky et al., 2023; Walton et al., 2023). For instance, prior to the Great Oxidation Event (GOE) at ca. 2.3 Ga, Archean ocean waters may have been characterized by pervasively anoxic and iron-


rich (ferruginous) conditions. The facility with which phosphate sorbs to iron oxides (Yoon et al., 2014), the precipitation of which would have been amplified by episodic oxidation of ferruginous ocean waters, may have further drawn down marine phosphate levels and muted the efficiency of P recycling between seafloor sediments and overlying ocean waters, resulting in higher biomass C:P ratios (Crowe et al., 2008; Jilbert and Slomp, 2013; Planavsky et al., 2023). The formation of green rust (GR; a mixed ferric/ferrous hydroxide) could have also impacted the availability of P under Archean conditions, as well as biomass C:P ratios (Xiong et al., 2023). However, the degree to which such environmental conditions during the Archean would have altered the elemental ratio of marine life remains largely unquantified, with some studies proposing that Archean oceans were characterized by higher, modern-like marine P concentrations (e.g., Rasmussen et al., 2023). Based on the current literature, there are wildly different views on the evolution of marine nutrient levels and the nutrient use of marine ecosystems.

Geochemical information embedded in ancient sedimentary rocks can provide novel insights into how the elemental stoichiometry of marine life has varied through time. Specifically, the C:P ratio of marine biomass would have strongly impacted the formation of

authigenic phosphate minerals—such as apatite [e.g., $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] and vivianite [e.g., $\text{Fe}_3(\text{PO}_4)_2$], which represent the largest burial flux of phosphorus in the modern oceans (Slomp et al., 1996; Ruttenger, 2003; Mort et al., 2010). For instance, the degradation of organic matter with a high C:P ratio in sediments should result in a relatively low rate of P release, which would result in a smaller dissolved sedimentary P pool and lower saturation indices of P-bearing minerals such as apatite and vivianite.

The Archean rock record contains a dearth of evidence for authigenic P minerals or strong P enrichments (Hofmann et al., 1991; Heimann et al., 2010). Given that post-depositional processes can convert authigenic P minerals into more thermally stable phases (like apatite) (Hao et al., 2019), the mineralogical signal for the formation of less stable P minerals such as vivianite can potentially be obscured. Nonetheless, Archean shales are characterized by high organic carbon to total P ($C_{\text{org}}:P$) ratios, which indicate low rates of authigenic P sequestration relative to the Phanerozoic (Reinhard et al., 2017; Planavsky et al., 2023; Sharoni and Halevy, 2022). At the same time, high total C:P ratios along with the overall absence of evidence for extensive authigenic apatite and vivianite in the Archean sedimentary rock record could be attributed to the lower availability of organic matter in the sediment. Evidence of widespread early diagenetic formation of iron(II) carbonate, siderite (FeCO_3) (Severmann et al., 2006; Fischer et al., 2009; Heimann et al., 2010), can provide additional windows into organic matter availability and porewater biogeochemical cycling. Although direct water-column siderite formation has been proposed (e.g., Jiang et al., 2022), this is directly at odds with extensive iron isotope data sets that indicate siderite formation occurred predominantly during early diagenesis (e.g., Heimann et al., 2010).

We use a sedimentary biogeochemical model that tracks the formation of the authi-

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genic P minerals apatite and vivianite along with siderite associated with various biomass C:P ratios. Our modeling results suggest that where the Archean sedimentary record shows evidence for the formation of siderite in the absence of vivianite (or strong P enrichments) this indicates that Archean marine primary producers were characterized by a C:P ratio of at least 500 mol:mol, approximately five times higher than the C:P ratios of average modern marine plankton. Strongly elevated C:P ratios in turn suggest extreme nutrient limitation of early Archean marine life.

MODEL DESCRIPTION

To bracket the possible range of biomass C:P ratios in the Archean oceans, we constructed a one-dimensional diagenetic model that simulates P sedimentary cycling. Specifically, by considering sources and sedimentary sinks for P, the model calculates the saturation of authigenic apatite and vivianite along with siderite at different organic matter C:P ratios. The full list of reactions for minerals and solutes included in the model, along with their rate formulations, are provided in Tables S1 and S2 in the Supplemental Material¹. The vertical distributions of P phases within the sediment are simulated at a steady state following a diagenetic equation (Berner, 1980):

$$0 = D_i \frac{\partial}{\partial x} \left(\varphi \frac{\partial C_i}{\partial x} \right) - \frac{\partial}{\partial x} (\varphi \nu C_i) + \sum_j R_{ij}, \quad (1)$$

¹Supplemental Material. Detailed description of the model. Please visit <https://doi.org/10.1130/GEOL.S.23881005> to access the supplemental material, and contact editing@geosociety.org with any questions.

where x is the depth below the sediment surface, C_i is the concentration of species i , D_i is the corresponding molecular diffusion coefficient corrected for sediment porosity φ , and ν is burial velocity. R_{ij} is the rate of reactions that consume or produce species i .

The main source of P in the sediment is the degradation of organic matter delivered from the water column, and its sinks include adsorption to iron oxide and precipitation as vivianite and apatite. Iron oxide dissolution is also a source of P to porewater (Berner, 1980). In order to be conservative, we do not explicitly represent this oxide-bound P release. The full description of the model, along with the kinetics of the reactions, are presented in the Supplemental Material. Finally, to account for the uncertainty involved in choosing the model input parameters, we adopt a stochastic approach, wherein the input parameters are randomly sampled from a reasonable range (reflecting published estimates) assuming a uniform distribution, and the model is then used to calculate the most probable range of values for saturation indices of vivianite, apatite, and siderite at different C:P ratios (model ranges are listed in Table S3). In the results shown here, the range of modeling and environmental parameters were changed within the range suggested in the literature and consistent with published observations of Archean stratigraphic records. For instance, the range of values for the flux of organic matter delivered to the seafloor was varied such that the amount of organic matter in the sediment, following early diagenetic reactions, as well as the isotopic composition of the produced pool of dissolved inorganic carbon (DIC), would be consistent with the range of total organic carbon (TOC) and carbon isotope

($\delta^{13}\text{C}$) values observed in Archean sedimentary records (Reinhard et al., 2017).

RESULTS AND DISCUSSION

Our results suggest that higher C:P ratios in marine biomass can potentially explain the absence of authigenic P enrichments (low vivianite and apatite formation) in the Archean rock record. Mechanistically, an increase in biomass C:P ratios would lead to a reduction in P release through organic matter degradation and consequently a smaller pool of P available for authigenic mineral formation. The diminished P pool would thermodynamically inhibit the formation of authigenic P minerals and result in a lower saturation index. Our results from the stochastic simulation provide compelling support for this framework: an increase in biomass C:P ratios—likely caused by lower availability of P in surface ocean waters—would have resulted in a considerable decrease in the saturation index of authigenic P minerals (Fig. 1). Our results indicate that, for a wide range of environmental input parameters (e.g., the magnitude of the organic matter flux), the formation of vivianite and apatite are thermodynamically inhibited at a C:P ratio above 500 mol:mol, almost five times higher than the canonical Redfield ratio (Fig. 1). According to our results, when the biomass C:P ratio is 1000 mol:mol, the saturation index of vivianite is between 0.5 and ~ -2.5 with a peak of ~ -1 . For apatite, the saturation index is between 0.5 and ~ -2 with a peak of ~ -1 . When the C:P ratio is 500 mol:mol, the modeled saturation index of vivianite is between 0.5 and approximately -2 with a peak of ~ -0.5 , and the saturation index of apatite is between 0.5 and ~ -1.5 with a peak of ~ -0.3 . The formation of siderite, on the other hand, is thermodynamically

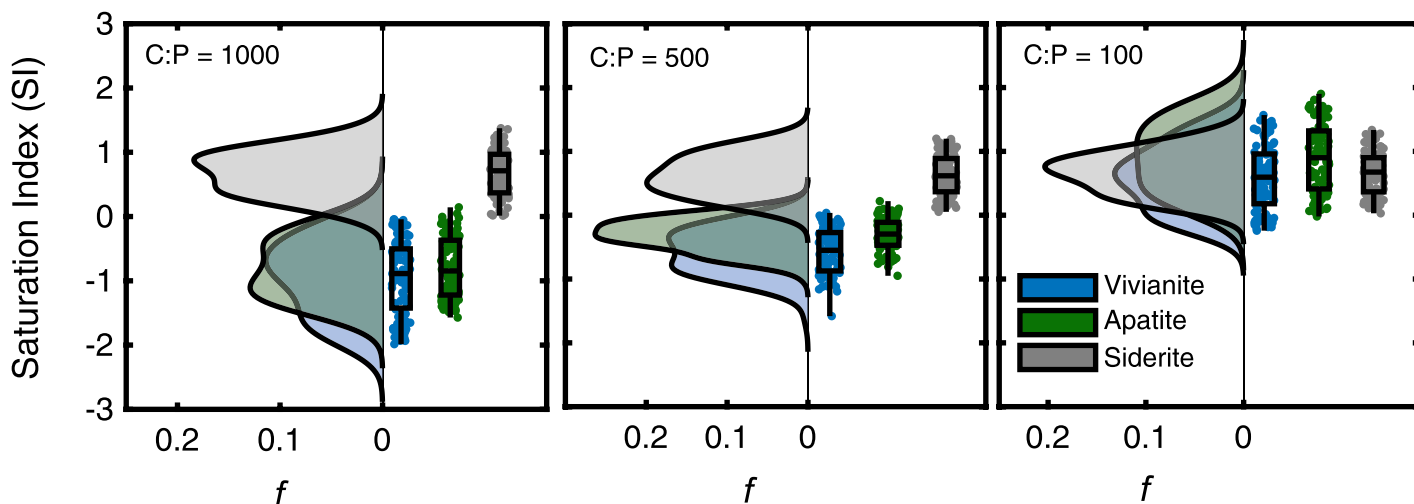


Figure 1. Modeled saturation indices for vivianite [$\text{Fe}_3(\text{PO}_4)_2$], siderite (FeCO_3), and apatite at different carbon (C) to phosphorus (P) ratios in marine biomass. Results show saturation indices at the bottom of the sediment column and were obtained from stochastic simulations where all model input parameters were sampled randomly assuming a uniform distribution, and the most probable ranges of saturation indices for vivianite, apatite, and siderite were obtained. The results indicate that the formation of vivianite and apatite should become thermodynamically inhibited at a C:P ratio above 500 mol:mol.

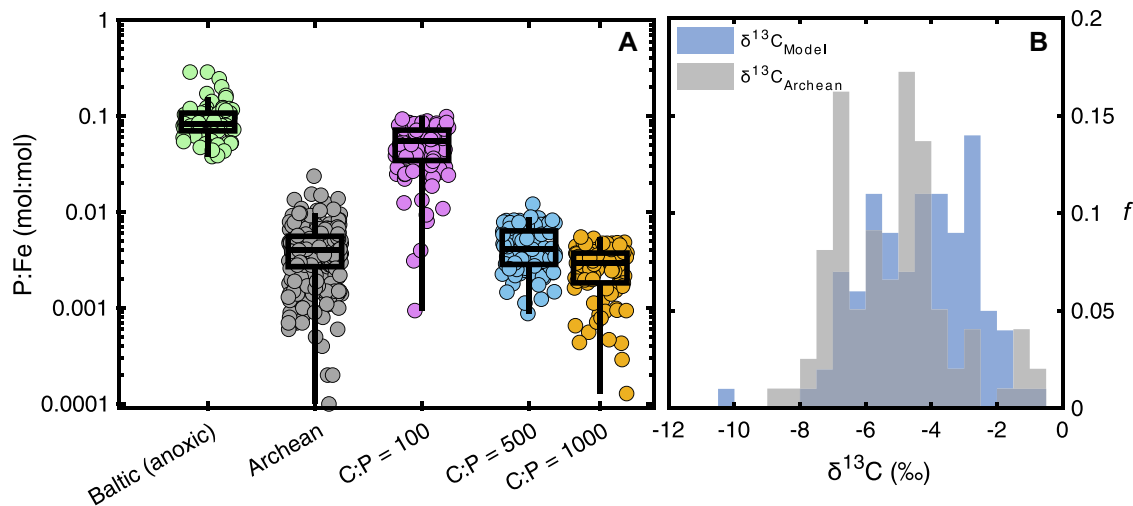


Figure 2. Validation of the model results against observations from the Archean rock record. (A) Comparison of the modeled P:Fe ratio to the observed P:Fe in the Archean rock record, as well as the modern anoxic Baltic Sea. Boxes correspond to interquartile range (IQR), which is the difference between the 75th and 25th percentiles of the data. (B) Results of the comparison [p -value (ANOVA) > 0.05] between the modeled carbon isotopic composition of dissolved inorganic carbon (DIC) and the observed $\delta^{13}\text{C}$ record (Fischer et al., 2009).

cally favorable under a wide range of environmental conditions, consistent with observations of siderite in Archean sedimentary successions (Hofmann et al., 1991; Rasmussen and Buick, 1999) (Fig. 1). Further, we find that for some relatively rare parameter combinations, the model achieves positive values for the saturation indices of vivianite and apatite even at high C:P ratios, which may explain recently described evidence of calcium-phosphate nanoparticles in an Archean iron formation (e.g., Rasmussen et al., 2023). Overall, however, our results suggest that, in most cases, the formation of these P minerals would still be thermodynamically inhibited, suggesting that authigenic apatite played a relatively minor role, at least relative to the modern, in the Archean P cycle (Fig. 1).

While our results are based on the calculation of saturation indices, it could be argued that the formation of vivianite was kinetically inhibited, and that vivianite could therefore have formed only at a relatively high saturation index. However, this argument is inconsistent with observations of modern anoxic environments. Observations from modern iron-rich anoxic waters, as the best modern analogs for the chemistry of Archean oceans, show that microbially mediated formation of vivianite proceeds at low to moderate saturation indices (Jilbert and Slomp, 2013; Cosmidis et al., 2014; Lenstra et al., 2018; Vuillemin et al., 2020). Specifically, results from iron-rich, low-sulfate Lake Towuti, Indonesia, suggest that vivianite can precipitate in the water column at sub- μM concentrations of P and near-zero saturation indices, indicating that vivianite formation is not strongly kinetically inhibited (Vuillemin et al., 2020).

Higher C:P ratios in early marine life are also consistent with observations from Archean sedimentary geochemical proxy records. Specifically, our stochastic simulation results suggest that P:Fe ratios and DIC $\delta^{13}\text{C}$ values generated by our model (e.g., as emergent properties) at

higher C:P ratios are consistent with observed Archean P:Fe ratios and carbonate $\delta^{13}\text{C}$ values (Yamaguchi et al., 2005; Fischer et al., 2009; Heimann et al., 2010) (Fig. 2). According to our results, the range of modeled P:Fe ratios associated with higher input biomass C:P ratios is statistically indistinguishable from empirically observed Archean P:Fe values [p -value (ANOVA) > 0.05], yet is significantly different from either observed P:Fe ratios in the modern anoxic Baltic Sea (Mort et al., 2010) or modern marine sediments in which biomass C:P ratios are close to the Redfield ratio (p -value < 0.05; Fig. 2A). While the large variation in recorded Archean P:Fe ratios can be explained by heterogeneity in environmental parameters that strongly shape authigenic processes, such as organic flux delivered to the seafloor and dissolved iron concentrations, this variability is largely consistent with the authigenic mineral P:Fe ratios that emerge from our stochastic simulations, in which the values of environmental model parameters were varied randomly within the range suggested by the literature (Table S3).

To further validate the range of organic matter flux values used in the model, we compared the results of the modeled $\delta^{13}\text{C}$ to the observed

$\delta^{13}\text{C}$ values from the Archean rock record (Fischer et al., 2009). Our results suggest no significant difference between modeled and geologically observed $\delta^{13}\text{C}$ values (p -value > 0.05). Building from previous work on the carbon isotope record (Heimann et al., 2010; although see Jiang et al., 2022), this supports the conclusion that higher biomass C:P ratios, rather than variability in the magnitude of the organic matter flux, can most readily explain the observed low phosphorus enrichments and the absence of vivianite in Archean sedimentary records (Fig. 2B). The conclusion of higher C:P ratios is also consistent with available data for the C:P ratio of organic matter in the sedimentary rock record, which indicates a higher C:P ratio during the Archean than in the Proterozoic and Phanerozoic (Fig. 3).

An alternative explanation for the absence of vivianite in the Archean record is, as noted above, the post-depositional transformation (e.g., during later diagenesis or metamorphism) of vivianite to apatite. In low-sulfate Archean oceans (Crowe et al., 2014), where the sulfide-induced dissolution of the vivianite (Vuillemin et al., 2013; Dijkstra et al., 2018) was unlikely to have been a major player in destroying vivianite

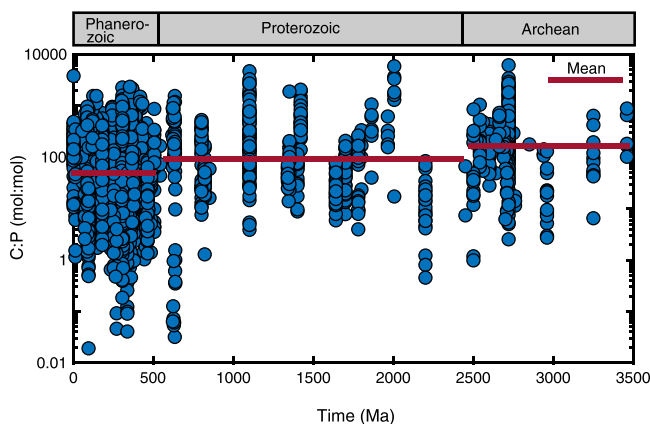


Figure 3. Organic carbon to phosphorus (C:P) ratios in marine siliciclastic sedimentary rocks. Red bars correspond to the average C:P ratios for each geologic time interval. Data are from Reinhard et al. (2017). The available data suggest a higher C:P ratio during the Archean and Proterozoic, implying a lower marine P concentration during these intervals of Earth's history.

records, the post-depositional transformation of vivianite to apatite was potentially important. More precisely, at elevated temperatures, the reaction of vivianite and calcite to form apatite and siderite (accompanied by dehydration reactions) would become thermodynamically favorable and likely act as a sink for vivianite during later diagenesis and metamorphism (Hao et al., 2020). Notably, it is likely that at a temperature above 100 °C, where the formation of apatite and siderite are still kinetically plausible, vivianite would metamorphose into apatite (Hao et al., 2020). Therefore, although vivianite may not be preserved in the rock record, the authigenic P (e.g., apatite) enrichment record is unlikely to have been strongly altered during metamorphism.

Observations from modern anoxic settings provide additional further support for markedly low Archean P enrichments (e.g., Planavsky et al., 2023). Specifically, observations from modern anoxic settings are indicative of a major role for vivianite in the overall P flux under anoxic conditions. For example, in iron-rich low-salinity estuaries along the Baltic Sea where the vivianite saturation index is near zero, vivianite precipitation accounts for as much as 40% of P removal from ambient waters (Lenstra et al., 2018), and P enrichments are commonly above 1%, higher than any of those observed in the Archean record.

CONCLUSIONS

By simulating the sedimentary P cycle under Archean-like conditions, we provide new insights into the longstanding question of whether early marine life was characterized by stoichiometric C:P ratios disparate from that of modern marine ecosystems. Taking a stochastic diagenetic modeling approach and drawing on previous plausible estimates informed by geologic archives for Archean marine conditions, we show that high biomass C:P values—departing from the canonical Redfield ratio—are required to explain the high sedimentary C:P ratios and low levels of vivianite and apatite in the Archean rock record. Specifically, while our results do suggest the rare formation of apatite under higher C:P ratios (e.g., Rasmussen et al., 2023), they also suggest that widespread formation of authigenic phosphorus minerals in sediments—both vivianite and apatite—was inhibited by the higher biomass C:P ratios of Archean marine communities.

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