Was There Really an Archean Phosphate Crisis?

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It has been suggested that sedimenting particles of ferric oxyhydroxide may have stripped dissolved phosphate from the ocean's photic zone during the Archean (1), when massive amounts of iron were deposited in the form of banded iron formations (BIF). Hypothesized phosphate concentrations of only 10 to 25% of the present-day values would have led to a reduction in phytoplankton productivity and, therefore, to lower rates of oxygen production and organic carbon burial. This model is predicated on the observation that ferric oxyhydroxide particles, resulting from the oxidation of Fe(II) in some modern submarine hydrothermal systems, sorb phosphate with a distribution coefficient (K_D) value of about 0.06 μM^{-1} (2).

However, compared with the modern ocean, the Archean ocean had substantially higher concentrations of dissolved silica, at least as high as at saturation with cristobalite (0.67 mM at 40°C in seawater) and possibly even at saturation with amorphous silica (2.20 mM) (3); modern oceans average <0.10 mM (4). Silica strongly sorbs to ferric oxyhydroxides, and, at the proposed concentration of phosphate in the Archean ocean [ranging from 0.03 to 0.29 μM (1)], silica could effectively compete with phosphate for available sorption sites [on the basis of α-FeOOH adsorption constants (5)]. Furthermore, iron-silica coprecipitation diminishes the resulting particle's point of zero net charge (PZNC) (6), rendering it less reactive to dissolved anions.

We determined the significance of high silica concentrations on phosphate sorption in two ways: (i) by using preformed ferrihydrite particles to demonstrate the competitive adsorption between silica and phosphate at different pH values and (ii) by oxidizing Fe(II) to precipitate ferrihydrite, in the presence of silica and phosphate, for the determination of K_D values (7). In the first instance, maximum phosphate adsorption onto preformed ferrihydrite particles occurs at pH < 7 and in the absence of silica (Fig. 1A); silica outcompetes phosphate as silica concentration increases. Furthermore, ferrihydrite incorporating silica shows a consistent decrease in PZNC (Fig. 1B) and correspondingly adsorbs even less phosphate (stippled lines in Fig. 1A).

Coprecipitation experiments with an initial Fe(II) concentration of 0.2 mM revealed that the presence of silica reduced the phosphate content of the resulting particles (Fig. 1C). In the complete absence of silica, we calculated a K_D value of 0.075 ± 0.003 μM^{-1}, similar to the K_D value used by Bjerrum and Canfield (1) for particles formed at modern submarine hydrothermal vents [compare with (2)], whereas K_D values decreased to 0.011 ± 0.004 μM^{-1} and 0.002 ± 0.002 μM^{-1} for solutions near cristobalite and amorphous silica saturation, respectively. Additionally, we observed silica to exert an even greater effect at lower dissolved Fe concentrations [0.02 mM Fe (fig. S6)]. Consequently, our calculated K_D values are conservative at 0.2 mM Fe, especially considering that previous estimates of dissolved Fe concentrations for the Archean ocean are around 0.05 mM (8). Only at much higher dissolved Fe concentrations (e.g., ~2 mM), such as in some hydrothermal vent fluids, does the effect of silica on phosphate sorption become negligible (fig. S6).

With the use of the P:Fe ratio in BIF as a proxy for dissolved phosphate concentrations in the Archean ocean [as the authors of (1) used, with whom we compare our data], we calculated that average dissolved phosphate concentrations would have ranged from 0.14 ± 0.01 μM (no silica) to 5.25 ± 2.63 μM in an amorphous silica-saturated ocean. The latter value is of the same order of magnitude as modern oceans (2.3 μM) (1). Importantly, there would have been diagenetic remobilization of phosphate during burial (probably leading to lower P:Fe ratios in BIF). Thus, the actual dissolved phosphate concentrations could have been even higher. If the Archean ocean contained abundant dissolved silica, as is generally believed, sedimenting ferrihydrite particles would not have been a major sink for phosphate. It is unlikely that there was a phosphate crisis, and a related reduction in phytoplankton productivity, caused by BIF deposition in the Archean ocean.

References and Notes

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Fig. 1. (**A**) Adsorption isotherms demonstrate, as a function of pH, the competition between silica and phosphate for the surface sites of ferrihydrite (solid lines) and silica-containing ferrihydrite particles (stippled lines). Data for ferrihydrite shown as circles; for particles formed in 0.67 mM SiO_2, triangles; and for particles formed in 2.20 mM SiO_2, squares. (**B**) Particles precipitated at various silica concentrations possess a lower PZNC than "pure" ferrihydrite as a result of silica incorporation. (**C**) Coprecipitation experiments performed at pH = 8 with 0.2 mM Fe(II) yield K_D values relating solid-phase and dissolved equilibrium phosphate concentrations. As a comparison to our results, data for modern deep-sea hydrothermal plumes [from (2)], and previously used to estimate Archean ocean phosphate concentrations (1), are plotted (plus signs). Also shown are the range of P/Fe(III) values in BIF [gray box; compare with (1)]. It is apparent from the coprecipitation data that the particles incorporate decreasing amounts of phosphate with increasing dissolved silica concentrations, and consequently the data suggest higher dissolved phosphate concentrations during BIF deposition.