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Mineralogical Controls on Phosphorus Cycling in the Precambrian Ferruginous Ocean

PRAGYA SINGH[1], YIJUN XIONG[2], BENJAMIN J. W. MILLS[3] AND SIMON W. POULTON[3]

[1]School of Earth, Environment and Sustainability, University of Leeds
[2]School of Earth and Environment, University of Leeds
[3]University of Leeds

Phosphorus (P) is widely recognised as the ultimate limiting nutrient on geological time scales, and hence P exerted a fundamental role in regulating global marine primary productivity, organic carbon burial, and ultimately the oxygen flux to the ocean-atmosphere system throughout the Precambrian Era (~4.6 – 0.541 billion years ago). Several geochemical proxies have been developed to reconstruct the Precambrian marine P reservoir and links to Earth's oxygenation history, but all have inherent limitations linked to uncertainty over key processes involved in P cycling. In particular, mineralogical controls on P cycling under anoxic ferruginous (Fe(II)-containing) conditions, which reflect the dominant redox state of the ocean throughout most of the Precambrian, are poorly understood. This limits our understanding of processes that led to the drawdown and retention of P in Precambrian anoxic environments. One such process concerns the extent of P uptake to (meta)stable, mixed-valence green rust, which has emerged as a key mineral precipitating in Precambrian ferruginous oceans, and the subsequent behaviour of P upon ageing to magnetite, a major iron-bearing mineral in both banded iron formations and ferruginous Precambrian shales. Here, we explore the control of carbonate green rust on bioavailable P and the fate of P upon mineralogical transformation of carbonate green rust into magnetite, through coprecipitation and mineral transformation experiments, at controlled pH under anoxic conditions. Our experiments demonstrate that P partitioning during carbonate green rust formation is strongly pH-sensitive, and we will discuss the role of green rust transformation pathways in controlling P cycling under conditions analogous to Precambrian ferruginous oceans.