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Impact of dissolved ferrous iron on phosphate adsorption: Revisiting the role of clay minerals in phosphorus cycling on early Earth

XING CUI[1], ZONGBIN ZHANG[2], JIHUA HAO[2], GUOCHUN ZHAO[1] AND MIN SUN[1]

[1]The University of Hong Kong
[2]University of Science and Technology of China
Presenting Author: cxing1124@163.com

Phosphorus is an essential nutrient for life that may play a crucial role in limiting primary productivity. Under anoxic conditions prevalent during Earth's early history, recent research highlighted the importance of clay minerals in delivering phosphorus through surface adsorption to the early ocean given the scarcity of iron (hydro)oxides. Notably, adsorption experiments revealed that a significant amount of phosphate adsorbed by clay minerals could be released when transitioning from the simulated acidic, diluted river water to more alkaline, saline seawater. However, these experiments have not taken into account the possible impact of elevated concentrations of dissolved ferrous iron (Fe^{2+}) in ferruginous waters persisting through early Earth on adsorption. In this study, we conducted batch adsorption experiments under anoxic conditions to simulate phosphate adsorption by clay minerals (e.g., kaolinite) in Archean marine and river water, emphasizing the influence of dissolved Fe^{2+}. Our preliminary findings suggest that the presence of moderate levels of dissolved Fe^{2+} relevant to early seawater greatly enhances phosphate adsorption onto kaolinite, which implies no phosphorus release from rivers to the ocean. It challenges the previously proposed "kaolinite shuttle" hypothesis that highlights the role of clay minerals as carriers for transporting phosphorus on early Earth.