Enhanced phosphorus regeneration in low oxygen marine settings: insights from modern and ancient sediments and implications for the future ocean

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Phosphorus (P) is a key nutrient for marine productivity and its availability plays a crucial role in the development of oxygen deficiency in marine systems. Most importantly, enhanced release of phosphate from seafloor sediments under low-oxygen conditions can drive a positive feedback loop between increased productivity, oxygen depletion and marine P availability. This feedback loop helps to sustain low oxygen conditions in restricted basins such as the Baltic Sea and may have contributed to the development of large-scale oceanic anoxia and massive burial of organic matter in the Earth's past. Here, we first summarize the field evidence for enhanced regeneration of P relative to organic carbon (C) from modern and ancient sediments. We then briefly review the responsible mechanisms, including enhanced regeneration of P from organic matter under low oxygen [1], and limited retention of P in inorganic minerals. We also present the results of an experimental investigation into the bacterial controls on P regeneration. Finally, we discuss the role that enhanced regeneration of P from sediments can play at the regional and global scale. We show that enhanced regeneration of P can account for the underestimation of phosphate concentrations in existing nutrient budgets of the Baltic Sea. Using biogeochemical ocean modeling, we show that oxygen depletion in the global ocean is also highly sensitive to the rate of enhanced regeneration of P. These results underline the need for improved quantitative and mechanistic understanding of the P cycle to better understand past changes in ocean oxygenation, and to predict those which may occur in the future.

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Ripening processes during crystallization of natrojarosite

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The crystallization behavior of jarosite type compounds $M\mathrm{Fe}_3$ $(\mathrm{SO}_4)_2$ $(\mathrm{OH})_6$ (M = Na^+, $\mathrm{H}_3\mathrm{O}^+$, K^+, Ag^+, NH_4^+) has received increasing attention due to the formation of these minerals in acid mine water drainage environments during the oxidation of sulphide minerals. The fact that jarosites were identified on Mars gives these minerals an additional interest as indicators of water-limited chemical weathering on that planet. Although different jarosite-type compounds have been synthetised by precipitation at temperatures close to 100°C [1], the genesis of these minerals in environmental conditions needs to be studied in depth. In this work, natrojarosite was synthesized by mixing 60 ml of Fe_3 $(\mathrm{SO}_4)_2$ (1N) and 40 ml of NaOH (1N) parent solution at 25 ± 0.1°C. Similar experiences were performed using 0.5N concentrations for both parent solutions (50:50 ratio). The experiments were carried out for specific reaction periods (1 day to 7 weeks) by keeping the solutions at constant agitation. The aging process of natrojarosite was followed by monitiring the precipitate crystallinity (X-ray diffraction), the aqueous solution composition (ICP-AES), and the pH.

Using 1N parent solutions, a low-crystallinity precipitate was obtained in the early stages of the experiments. However, as the reaction time passes by, the main XRD reflections (012, 021 and 113) of natrojarosite become more apparent and undergo a progressive decrease of widthness (FWHM) and an increase of intensity which indicate an increasing degree of crystallinity. In contrast, using 0.5N parent solutions the precipitate remained amorphous during the whole aging process. The pH values varied between 2.6 and 2.2, in all experiments. The aqueous solution exhibited a slight increase of both Fe and Na concentrations that is consistent with the development of the crystalline phase. Aqueous solution modellization (phreeqc code) evidenced higher saturation indices for hematite than for natrojarosite, which indicates that the formation of natrojarosite was governed by kinetic factors.

[1] J.E. Dutrizac & S Kaiman (1976) *Canadian Mineralogist* **14**, 151–158.