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Vivianite blues

From Dutch painters to ocean sediments, Caroline Slomp discusses the role vivianite plays in the distribution of phosphorus, an essential nutrient for life.

Excavated bones, soils or sediments seemingly splashed with blue paint – archaeologists and geologists will immediately recognize the mineral vivianite, a hydrated ferrous–iron phosphate mineral. Vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$] is colourless when it forms but, upon exposure to oxygen and light, its colour changes to a vivid bright blue, followed by lighter or darker hues that may even transform to yellow–browns and greys. These colour changes are the result of the oxidation of iron during the conversion of vivianite to a range of other iron-phosphate minerals[1–3]. For Dutch painters in the 17th century that used vivianite as a pigment, including Johannes Vermeer and Rembrandt van Rijn, this evanescent property posed various challenges[2]. Just imagine selecting vivianite to portray a brilliant blue sky on your canvas and then, once finished, realise that the painted sky gradually changes to a dull grey.

The ephemeral properties of vivianite explain why this mineral often eludes detection in natural environments. Phosphorus is a key nutrient that is unavailable for plant growth when fixed in minerals, making it important to know where and how phosphorus-bearing minerals form. Until recently, apatite, a calcium-phosphate mineral, was considered the dominant phosphorus mineral in soils and sediments. Careful sample handling to prevent oxidation occurring and the development of more powerful analytical methods, including a range of X-ray techniques, has altered this view. We now know that vivianite is a rather common phosphorus mineral in sediments of lakes and estuaries[1,4]. Vivianite is also abundant in iron-rich lakes seen as analogues of the ocean in the geological past[5,6]. We should not overlook vivianite when trying to understand Earth's phosphorus cycle.

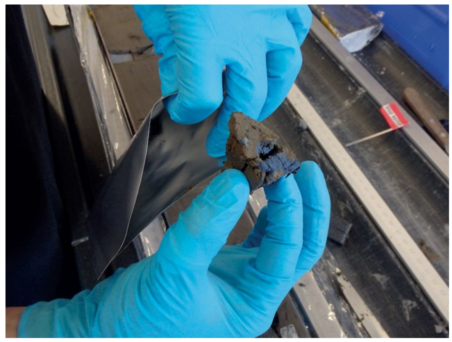

Fig. 1 | Vivianite mineral. Vivianite from a drill core of Baltic Sea sediment collected during Expedition 347 for the International Ocean Discovery Program.

Vivianite forms in oxygen- and hydrogen sulfide-free sedimentary environments where concentrations of dissolved phosphate and ferrous iron are high. Decaying organic matter is usually the main source of the phosphate, although apatite in bones may also convert to vivianite. Dissolved iron is sourced from iron oxides and, in archaeological soils, also from ironware[1,3]. Microbes play an indirect role in vivianite formation by driving iron and phosphorus release into solution. In some cases, they can also play a direct role by precipitating vivianite in their cells[1,5]. Some of the iron in vivianite can be replaced by other cations, such as magnesium or manganese. Such inclusions may impact the solubility of the mineral[4] and allow sedimentary vivianite to be distinguished from that formed in other geological settings[1,2].

Vivianite was long thought to be absent from marine sediments because the mineral dissolves readily in the presence of hydrogen sulfide. Seawater is rich in sulfate, which is converted to hydrogen sulfide as organic matter in oxygen-free sediments degrades. Hydrogen sulfide, in turn, may be removed as iron sulfide. Hence, it is the balance between the supply of iron and sulfide in marine sediments that determines if there are stable niches for vivianite formation (Fig. 1).

This balance is particularly important in coastal systems suffering from eutrophication, where an excess of nutrients (usually nitrogen or phosphorus) is associated with elevated algal growth that can damage water quality and kill off other aquatic life. Eutrophication of coastal systems can be avoided by not letting phosphorus-rich wastewater leak into the sea. One way to achieve this is to increase the removal of phosphorus by trapping it as vivianite. Our knowledge of the drivers of vivianite formation may be harnessed to achieve that goal, with efforts already underway to optimize the formation of vivianite in wastewater treatment plants. Besides avoiding nutrient pollution, the vivianite minerals harvested from wastewater treatment plants could also be used as agricultural fertilizer[7], thereby nicely closing the terrestrial phosphorus cycle.

While vivianite is clearly not the pigment of choice for painting blue skies, its formation and fate are key to understanding and protecting nutrient cycling in Earth's surface environments.

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Competing interests

The author declares no competing interests.

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