Coupled cycling of Mn and micronutrients in marine sediments

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Manganese (Mn) oxides are ubiquitous in oxic marine sediments and play a fundamental role in the biogeochemical cycling of micronutrient trace-metals in the ocean [1]. In the modern oceans, for example, Mn oxides provide the dominant sedimentary sink for the micronutrient nickel (Ni) [2], where Ni concentration in seawater is coupled to an equilibrium reaction between dissolved Ni and the Mn oxide birnessite [3]. In addition to this phyllomanganate phase, the other main Mn bearing phases in marine sediments are the phyllomanganate buserite and the tectomanganate todorokite [4]. In the environment, these Mn(III/IV) oxides are thought to form via the microbial oxidation of Mn(II) [5], however, although todorokite is often found intimately associated with phyllomanganates in ferromanganese precipitates, it is widely regarded as a neo-formed phase, formed during the transformation of an authigenic phyllomanganate under diagenetic and mild hydrothermal conditions [6]. In this regard, across significant areas of the seafloor, birnessite and buserite are transient mineral phases. This is important because the long-term fate and mobility of dissolved micronutrients scavenged by authigenic Mn oxides will depend on how these phases transform, and whether scavenged micronutrients are retained by neo-formed todorokite or released to sediment porewaters.

The presence of trace-metal impurities in authigenic phyllomanganates is traditionally believed to aid their recrystallization to todorokite, with the impurities eventually retained in the neo-formed mineral structure [6]. Here, with combined experimental and natural sample work, we show that, in fact, Ni significantly retards the transformation of birnessite to todorokite under diagenetic and mild hydrothermal conditions, and is ultimately released to porewaters from todorokite during a late stage dissolution recrystallization process [7]. The diagenesis of marine Mn oxides might therefore provide a significant benthic source of micronutrients to seawater [7].

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