Early diagenetic formation of magnesian vivianite nodules in sediments off SW Taiwan

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Ferromagnesian phosphate nodules occur in hemipelagic iron-rich sediments cored from the Formosa Ridge (FMR, core length ca. 29 m), Yungan Ridge (YAR, 24.2 m), SE YAR (25.6 m), Kaoping Canyon (KPC, 38 m), and Lower Fengliao Basin (LFLB, 15.7 m) off SW Taiwan with the sulfatemethane transition (SMT) zone at 8.9, 5.0, 2.5, 8.5, and 11.0 mbsf, respectively. The phosphate is magnesian vivianite or baricite, having 37-85 mol% vivianite, 15-63 mol% bobierrite, and <6 mol% reddingite, distinctly different from vivianite in freshwater sediments. Scavenging of downward diffusive dissolved sulfide by forming acid volatile sulfide (AVS) or pyrite in a sulfidization zone could have favored prominent mineralization of vivianite below the sulfidization front in the YAR sediments. Without a record of intense sulfidization driven by anaerobic oxidation of methane (AOM) in the FMR and KPC sediments, the downcore distribution of magnesian vivianite nodules is scattered below the present-day SMT zone and the vivianite occurs in the presence of AVS and siderite with limited growth of pyrite and has a relatively narrow range of iron-rich composition, indicating relatively steady growth in reducing environments at depth. In the transition zone from the zone of vivianite mineralization to the overlying sulfidization zone in the YAR sediments, there are alternate growths of iron sulfides and vivianite and Fe- and Mg-enriched zoning in individual vivianite nodules due to fluctuations of the sulfidization front and methane flux, while similar features in the FMR and KPC sediments at some depths may be attributed to temporal variations of weak diffusive methane flux and AOM under conditions of low dissolved sulfate concentrations at depth. Formation of vivianite in the LFLB sediments is spotty as well but is in a depth interval sandwiched between an overlying AVS-dominated zone and the present SMT zone with a underlying zone of intense pyrite crystallization possibly marking a past SMT record. The result suggests that early diagenetic magnesian vivianite can occur in reductive marine sediments, particularly in those that have high reactive-iron contents and high sedimentation rates permitting evasion from early sulfidization due to AOM in the SMT zone, and adds to the increasing volume of evidence to support that magnesian vivianite can be an important P sink in marine environments.