# Authigenesis of vivianite as influenced by methane-induced sulfidization in cold-seep sediments off southwestern Taiwan

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### ABSTRACT

Authigenesis of iron-rich phosphate nodules occurs in iron-rich cold-seep sediments (MD052911 core) at Yung-An Ridge offshore southwestern Taiwan. Raman, FTIR, and quantitative X-ray energy-dispersive spectroscopic analyses indicate that the phosphate mineral is vivianite (or barićite) and shows Fe/Mg molar ratios spanning from *ca.* 0.6 to 4.0 and a general down core trend of increasing Fe/Mg ratios. The formation of vivianite is limited to a depth interval of 13–17 mbsf (meters below seafloor) and is most prominent at ~16 mbsf in association with high dissolved iron concentrations and depleted dissolved sulfide below a peak sulfidization zone (enriched in mackinawite and greigite). Alternate growths of vivianite and iron monosulfides and compositional zoning with Mg enriched towards the peripheries of individual nodules occur in the transition from the zone of vivianite mineralization to the sulfidization zone. The crystallization of vivianite below the sulfidization front could have been favored by scavenging of downward diffusive dissolved sulfide from pore waters in the sulfidization zone. Alternate growths and overlapping of the zones of iron monosulfides and vivianite can be attributed to fluctuations of the sulfidization front and methane flux. The discovery of vivianite in the Yung-An Ridge sediments implies that authigenic vivianite can be an important sink for phosphorus burial in cold-seep sediments that have high reactive-iron contents and high sedimentation rates.

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## 1. Introduction

Vivianite which has an ideal formula of $Fe_3^{2+}(PO_4)_2 \cdot 8H_2O$ has been found in lacustrine sediments (Fagel et al., 2005; Gächter and Müeller, 2003; Nriagu and Dell, 1974; Sapota et al., 2006), riverine sediments (Hearn et al., 1983), estuarine sediments (Postma, 1982), low-temperature hydrothermal deposits (Liferovich et al., 2001; Robertson, 1982; Rodgers et al., 1993), soil systems (Walpersdorf et al., 2013), and marine sediments (e.g., Burns, 1997). It is probably the most stable Fe(II) orthophosphate in sediments formed in reducing environments with high $Fe^{2+}$ and $HPO_4^{2-}$ activities (Nriagu, 1972). Vivianite has rarely been reported to occur in marine sediments as even low sulfide activities are unfavorable to its formation. In marine systems, high concentrations of hydrogen sulfide are commonly produced from bacterial sulfate reduction associated with degradation of organic matter and anaerobic oxidation of methane (AOM), leading to formation of pyrite or other iron sulfides (Berner, 1970, 1984).

Vivianite may have an allochthonous origin in marine sediments, with abrasion and dissolution features on crystal surfaces as seen in vivianite nodules from the eastern continental margin of India (Rao et al., 1992). These allochthonus vivianite nodules were considered to be formed in estuarine regions and transported to the continental slope by gravity flows. Authigenesis of vivianite or Fe(II) phosphates in marine sediments has been suggested in a few studies (Burns, 1997; Jilbert and Slomp, 2013; Martens et al., 1978; März et al., 2008; Ruttenberg and Goñi, 1997; Schulz et al., 1994; Slomp et al., 2013). The formation of vivianite or Fe(II) phosphates in marine sediments is often associated with internal redistribution of organic and inorganic P-bearing species and high dissolved Fe concentrations in pore waters below the sulfate-methane transition (SMT) zone such as the cases of the Amazon Fan (Burns, 1997; Ruttenberg and Goñi, 1997) and the Zambezi deep-sea fan (März et al., 2008). However, a recent study on authigenic phosphorus (P) minerals in the euxinic basins of the Baltic Sea suggested that Fe(II) phosphates could form within the SMT zone due to high $HPO_4^{2-}$ concentrations in microenvironments (Jilbert and Slomp, 2013). Accumulation and subsequent reduction of P-bearing iron or manganese oxides were considered important for Fe(II)-phosphate formation in the aforementioned studies. The

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authigenesis of vivianite or Fe(II) phosphates could contribute to P burial and cycling in marine sediments, but only very limited data with respect to detailed chemical and textural properties of such iron phosphates are available in the literature.

Sand-sized vivianite nodules were recently discovered in core sediments from Yung-An Ridge (YAR) (Hsu and Jiang, 2008) which has been regarded as one of the major gas-hydrate promising reservoirs offshore southwestern Taiwan, showing prominent signals of bottom simulating reflectors (BSRs) and methane activities (Liu et al., 2006; Chuang et al., 2006, 2010). The muddy hemipelagic YAR sediments have been under the influence of high methane fluxes with an SMT zone at ~5 mbsf (meters below seafloor) and a sulfidization front signified by a peak of acid volatile sulfide (AVS) in 10–15 mbsf (Lim et al., 2011). The YAR may represent a distinguished geochemical setting for the crystallization of Fe(II)-phosphate minerals in marine sediments. This study characterizes the vivianite utilizing electron microscopic and spectroscopic techniques. The purpose is to report its occurrence and microtextural and compositional properties that are not well known for iron phosphate minerals in marine sediments elsewhere. Possible formation processes of the mineral are discussed based on the present mineralogical result and the pore-water and sediment chemistry reported previously (Lim et al., 2011).

## 2. Geological setting

The area off southwestern Taiwan between ~21.5°N and ~23°N is in an initial stage of arc-continent collision. It includes an overriding syn-collision accretionary prism that coalesces with the Luzon arc in the east and borders the Manila trench and a deformation front adjoining the underthrusting Eurasian lithosphere (South China Sea) in the west (Huang et al., 1997, 2000). The accretionary wedge consists of three structural domains (Fig. 1) including the lower slope, the upper slope, and the backthrust domains from west to east (Reed et al., 1992). The boundary between the lower slope and the upper slope domains is located at the eastern bank of the NNE-trending Kaoping canyon. The lower slope domain consists of a series of bathymetric ridges related to active thrusting and folding (Lin et al., 2008). Widely distributed BSRs (Chi et al., 1998; Chow et al., 2000; Liu et al., 2006) and cold seeps with high methane concentrations in bottom and pore waters were detected

in the lower slope domain (Lin et al., 2006; Chuang et al., 2006, 2010). The upper slope domain is characterized by steeply-dipping or intense deformation of accreted strata as evidenced by highly discontinuous and low-amplitude seismic reflections, with relatively smooth seafloor topography implying inactive faulting in recent time (Reed et al., 1992; Lin et al., 2009a). However, submarine mud volcanoes and diapirs and gassy sediments were reported with chirp sonar and seismic reflection data at many sites in the upper slope domain (Chiu et al., 2006). The backthrust domain is located at the eastern border of the accretionary wedge, mainly consisting of eastward thrust faults (Reed et al., 1992; Chi et al., 2003). The geological framework and detailed tectonic features of the incipient arc-continental collision zone can be found elsewhere (Huang et al., 1997, 2000; Liu et al., 1997, 2006; Lin et al., 2008, 2009).

The occurrence of BSRs and gas hydrates in the upper and lower slope domains was suggested to be structurally controlled (Liu et al., 2006; Lin et al., 2009b; Schnürle et al., 2011). High concentrations of methane and steep sulfate gradients in pore waters as well as shallow SMT zones, high pyrite contents, and authigenic carbonates were detected in sediments at many core sites in the region, including the YAR sediments (Chuang et al., 2006, 2010, 2013; Lin et al., 2006; Lim et al., 2011).

The studied core site MD052911 is located at YAR (Fig. 1) which is one of the thrust ridges in the lower slope domain (Lin et al., 2008). Distinguished BSR signals in seismic profiles are indicative of gas-hydrate and free-gas occurrence beneath the ridge sediments (Liu et al., 2006). In addition, chemosynthetic vent communities, gas plumes, and $\delta^{13}$C-depleted authigenic carbonates were found in the ridge area (Huang et al., 2006; Lim et al., 2011; Lin et al., 2009c).

Variations in pore-water and sediment chemistry of the MD052911 core suggest that the MD052911 core site is an active methane-venting spot with oscillation records of pyrite abundance influenced by temporal changes of methane flux (Lim et al., 2011). Three zones with diverse characteristics of pore-water and sediment compositions were identified (Fig. 2). The upper section (<10 mbsf) is characterized by an SMT zone at ~5 mbsf, relatively high pyrite contents, comparatively low concentrations of dissolved iron, and high levels of dissolved sulfides peaked at ~5 mbsf. The middle section (10–20 mbsf) is marked by high AVS contents particularly in 10–15 mbsf, elevated concentrations of dissolved iron in 15–20 mbsf, low pyrite contents, and high levels of oxalate-extractable iron (reactive iron) (Lim et al., 2011). Distinctly high pyrite and carbonate contents are characteristic of the lower section sediments (>20 mbsf). The elevated pyrite content associated with the formation of carbonate minerals indicates a temporal record of AOM controlled by methane flux fluctuations (Lim et al., 2011).

## 3. Materials and methods

### 3.1. Sampling

A sediment core of 2389 cm in length was collected at site MD052911 (22°15.617′N, 119°51.079′E) on the southwestern flank of the Yung-An Ridge (Fig. 1), using a giant piston corer (the Calypso system) on the research vessel Marion Dufresne during a cruise in May 2005. The water depth was 1076 m.

Measurements for the concentrations of methane in wet sediments (sampled onboard utilizing the headspace method), dissolved sulfate, sulfide, and iron in pore waters (collected onboard by centrifugation and filtering), and total organic carbon, total organic nitrogen, pyrite sulfur, AVS, total iron, and oxalate extractable iron in sediments (freeze-dried before analysis) were
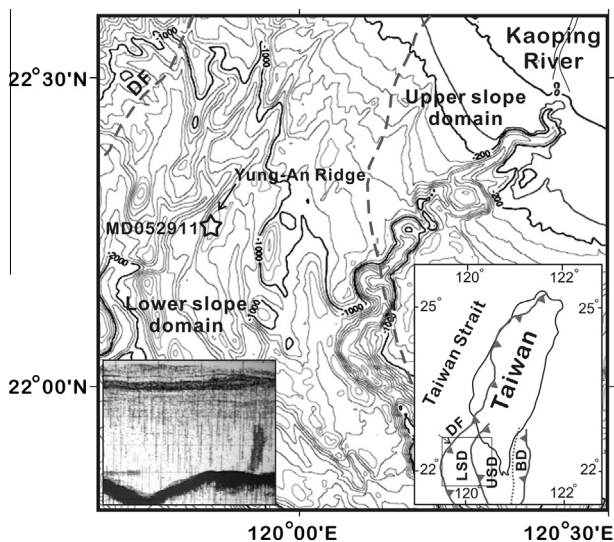


**Fig. 1.** Bathymetric map showing the MD052911 site in the gas hydrate-promising area off southwestern Taiwan. The left insert is an acoustic image displaying flare signals due to gas plumes at the Yung-An Ridge. DF = deformation front; LSD = lower slope domain; USD = upper slope domain; BD = backthrust domain.