A novel authigenic magnetite source for sedimentary magnetization

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ABSTRACT

We report a novel authigenic nanoscale magnetite source in marine methane seep sediments. The magnetite occurs in large concentrations in multiple horizons in a 230 m sediment core with gas hydrate–bearing intervals. In contrast to typical biogenic magnetite produced by magnetotactic bacteria and dissimilatory iron-reducing bacteria, most particles have sizes of 200–800 nm and many are aligned in distinctive structures that resemble microbial precipitates. The magnetite is interpreted to be a byproduct of microbial iron reduction within methane sediments with rapidly changing redox conditions. Iron sulfides that accumulated at a shallow sulfate-methane transition zone were oxidized after methane seepage intensity decreased. The alteration process produced secondary iron (oxyhydr)oxides that then became a reactive iron source for magnetite authigenesis when methane seepage increased again. This interpretation is consistent with 13C depletion in coexisting carbonate nodules. The authigenic magnetite will record younger palaeomagnetic signals than surrounding sediments, which is important for palaeomagnetic interpretations in seep systems. The microbial and possibly abiotic processes that caused these magnetic minerals to form at moderate burial depths remain to be determined.

INTRODUCTION

Magnetic signals preserved in sediments provide fundamental information for ancient tectonic, geomagnetic field, and environmental reconstructions. Sedimentary magnetic signals have traditionally been thought to be dominated by detrital magnetic iron-oxide particles, while biogenic magnetite with magnetically ideal stable single-domain (SD) properties has proven more recently to be a significant recorder of strong and stable sedimentary remanences over geological time scales (Chang and Kirschvink, 1989; Kopp and Kirschvink, 2008; Roberts et al., 2012). There are two main pathways for biomeralization of ultrafine biogenic magnetite in sediments, one of which is used by magnetotactic bacteria (MTB) and the other by dissimilatory iron-reducing bacteria (DIRB) (Moskowitz, 1995; Roberts, 2015). Intracellular magnetite produced by MTB has well-defined sizes, morphologies, chain arrangements, and stoichiometries (Devouard et al., 1998; Kopp and Kirschvink, 2008). The magnetic nanoparticulate remains of MTB are preserved post-mortem as magnetofossils and are found in diverse sedimentary environments (Chang and Kirschvink, 1989). In contrast, extracellular authigenic magnetite produced by DIRB (Lovley et al., 1987) is thought to have sizes <20 nm in diameter (Li et al., 2009) with magnetically unstable superparamagnetic properties (Moskowitz et al., 1993). Although dissimilatory iron reducers occur widely in anoxic subsurface sediments, geological preservation of extracellular magnetite has been documented only rarely (e.g., Roberts, 2015).

MAGNETIC SIGNALS RECORDED IN METHANIC SEDIMENTS

The study site GMGS2-16 is situated on the passive continental margin of the northern South China Sea (Fig. 1), which contains large basins with thick sedimentary sequences that have been deformed by movement along tectonic lineaments (McDonnell et al., 2000). Abundant methane-derived carbonates and gas hydrates (Fig. 1) confirm that methane seepage occurs widely in the study area (see the Supplemental Material for materials and methods).

Mass magnetic susceptibility (χ) of sediments in core GMGS2-16 has large variations

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(Fig. 2A). Peak \( \chi \) values (>\( 2 \times 10^{-4} \) m\(^3\) kg\(^{-1}\)) occur in multiple layers with nodular magnetic mineral aggregates (Figs. 3A and 3B; Fig. S1 in the Supplemental Material). In contrast, \( \chi \) has low and constant values of \( \sim 1.0 \times 10^{-4} \) m\(^3\) kg\(^{-1}\) in intervals without magnetic aggregates.

To characterize the magnetic domain state and magnetostatic interactions of magnetic particles, first-order reversal curve (FORC) measurements (Pike et al., 1999) were produced for bulk sediments. FORC diagrams for low-\( \chi \) samples reveal a low-coercivity component and a magnetostatically interacting higher-coercivity SD component (Fig. 2E1; Figs. S2A–S2C); the latter is typical of greigite-bearing sediments that have experienced...
diagenetic sulfidization and magnetic dissolution (Roberts et al., 2018). In contrast, similar FORC diagrams were produced for samples with peak $\chi$ values (Figs. 2E2–2E4; Fig. S2D), which indicate the presence of stable SD particles with strong magnetostatic interactions and/or vortex-state particles (see Roberts et al. [2017] for signatures of vortex-state particles). Equidimensional SD magnetite has sizes in the $\sim 20$–75 nm range, and vortex-state particles have sizes in the hundreds of nanometers range (Muxworthy and Williams, 2009).

- X-ray diffraction (XRD) analysis reveals that magnetite is the sole magnetic phase in the magnetic mineral extracts (Fig. 2F). This was confirmed by observations of clustered ultrafine particles within the magnetite aggregates, which range mainly from 200 to 800 nm in size (Fig. 3; Fig. DR3). Rarely, aligned magnetite particles were found (Figs. 3E and 3F; Figs. S3F–S3H), which differ from magnetofossil chains and are more similar to microbially formed structures (e.g., Johannessen et al., 2020). Individual particles are mainly spherical (Fig. 3G) or clustered euhedral crystals (Figs. 3H and 3I). Both particle types also occur as smaller nanocrystals (Figs. 3G–3I) with single-crystal sizes ranging from 10 to 20 nm (Figs. 3J–3L).

**NATURE OF THE MAGNETITE NANOPARTICLES**

Magnetite in marine sediments generally originates from detrital inputs from land or as an authigenic mineral that forms during diagenesis (Roberts, 2015). The ultrafine, well-crystallized, and aggregated nature of the studied particles...
expected to be reduced in sulfidic environments. This is unusual because magnetite is the identified authigenic magnetite accumulated (cf. Chen et al., 2016; Lin et al., 2018). Most of \( \delta^{2016} \), co-occurrence of bivalve shells, and low enrichments in carbonate nodules (Chen et al., 2016) would also promote iron-sulfide mineral oxidation. Wüstite (Roberts, 2015). Abundant euhedral magnetite in such a sulfidic environment is puzzling and indicates that magnetite formation postdated most of the carbonate and pyrite formation at paleo-SMTZs, after the environment became hydrogen sulfide limited.

We propose the following scenario for magnetite authigenesis driven by microbial iron reduction within methanic sediments that undergo dynamic methane seepage changes (Fig. 4). Vertical SMTZ movement and variable redox conditions occur commonly in this gas hydrate-bearing area (Z. Lin et al., 2016). In initial stages with high methane fluxes, sulfide production would cause pyrite accumulation at a shallow SMTZ. When seepage diminishes, downward-moving, seawater-derived oxidizing fluids would promote iron-sulfide mineral oxidation at the former SMTZ, leading to secondary iron (oxyhydr)oxide formation at paleo-SMTZs. Gypsum formation (Q. Lin et al., 2016). High porosity and permeability in coarse sediments (Chen et al., 2016) and advective seawater transport due to convective fluxes at seeps (Aloisi et al., 2004) would facilitate sulfide mineral oxidation.

An ensuing change fromoxic to methanic environments would then have been caused by a resurgence of high methane fluxes (Lin et al., 2018). Rapid sediment burial (e.g., mass wasting; Wang et al., 2016) would also promote iron (oxyhydr)oxide preservation during burial into a methanic environment. The presence of wüstite (FeO; Fig. 2F) suggests a sulfide-free Fe\(^{2+}\)-rich environment (cf. Kolo et al., 2009) and also indicates rapid burial of reactive iron (oxyhydr) oxides without further alteration by sulfidization.

Magnetite authigenesis has not been identified previously in methanic sediments, although microbial iron reduction is observed commonly in similar sedimentary settings (Egger et al., 2014; Riedinger et al., 2014; Amiel et al., 2020). Microbial iron reduction in methanic zones can be driven by (1) DIRB outcompeting methanogens for organic substrates (Thamdrup, 2000), (2) methanogens that switch from methanogenesis to iron reduction with an unidentified electron donor that does not appear to be methane (Sivan et al., 2016), or (3) iron reduction coupled to anaerobic oxidation of methane (Beal et al., 2009; Egger et al., 2014). Extracellular titanomagnetite has been identified under nearly natural methanic conditions in culture with the archaean *Methanosarcina Barkeri* (Shang et al., 2020). Based on this observation, microbiologically driven magnetite authigenesis with iron (oxyhydr)oxides as an electron acceptor (Fig. 3B; Fig. S1) could be feasible in methanic sediments. Organic substrates for dissimilatory iron reduction are probably scarce when these sediments are subjected to methanic conditions, which suggests that coupling of iron reduction to anaerobic oxidation of methane is the most likely process. Although the nature of iron reduction in methanic sediments is not clear, the presence of both microorganisms with iron reducing abilities and reactive Fe\(^{2+}\)-bearing minerals is essential for the process to occur. Methanogenic and/or methanotrophic archaea are present throughout the studied core (Cui et al., 2019). The presence of iron (oxyhydr)oxides in methanic sediments at site GMGS2-16 would, thus, allow authigenic magnetite formation by microbial iron reduction. Irrespective of the lack of laboratory culture studies of magnetite formation mechanisms in methanic sediments, the proposed scenario...
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