Formation of diagenetic siderite in modern ferruginous sediments

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ABSTRACT

Ferruginous conditions prevailed in the world’s deep oceans during the Archean and Proterozoic Eons. Sedimentary iron formations deposited at that time may provide an important record of environmental conditions, yet linking the chemistry and mineralogy of these sedimentary rocks to depositional conditions remains a challenge due to a dearth of information about the processes by which minerals form in analogous modern environments. We identified siderites in ferruginous Lake Towuti, Indonesia, which we characterized using high-resolution microscopic and spectroscopic imaging combined with microchemical and geochemical analyses. We infer early diagenetic growth of siderite crystals as a response to sedimentary organic carbon degradation and the accumulation of dissolved inorganic carbon in pore waters. We suggest that siderite formation proceeds through syntaxial growth on preexisting siderite crystals, or possibly through aging of precursor carbonate green rust. Crystal growth ultimately leads to spar-sized (50 μm) mosaic single siderite crystals that form twins, bundles, and spheroidal aggregates during burial. Early-formed carbonate was detectable through microchemical zonation and the possible presence of residual phases trapped in siderite interstices. This suggests that such microchemical zonation and mineral inclusions may be used to infer siderite growth histories in ancient sedimentary rocks including sedimentary iron formations.

INTRODUCTION

Ancient sedimentary iron formations (IFs) are composed of diverse iron oxides, silicates, and carbonates that are thought to form through diagenesis and subsequent metamorphism of primary ferric-ferrous (Fe3+/Fe2+) iron (oxyhydr)oxide precipitates (Gole, 1980; Raiswell et al., 2011). Yet iron carbonate minerals such as siderite (FeCO3) are also thought to form as primary pelagic precipitates (Canfield et al., 2008; Bekker et al., 2014), and their mineralogy has been used to infer atmospheric and oceanic conditions on early Earth (Holland, 2006). The interpretation of IFs and their depositional conditions depends on our knowledge of their mineral origins and formation pathways (Ohmoto et al., 2004), which is limited in part due to scarcity of analogous ferruginous (Fe-rich, SO4-poor) environments on Earth today (Konhauser et al., 2005; Posth et al., 2014). Ferruginous sediments are deposited in the Malili Lakes, a chain of five interconnected tectonic lakes on Sulawesi Island, Indonesia (Haffner et al., 2001). Erosion of ultramafic rocks and lateritic soils in the Malili Lakes catchment supplies considerable amounts of iron (oxyhydr)oxides but little sulfate to the lakes (Crowe et al., 2004; Morlock et al., 2019). Lake Towuti (2°45’00”S, 121°30’00”E) is currently stratified with anoxic conditions below 130 m (Costa et al., 2015; Vuillemin et al., 2016). In nearby Lake Matano (2°29’77”S, 121°20’00”E), carbonate green rust (GR) forms below the chemocline, likely via the reduction of ferrihydrite or via its reaction with dissolved Fe3+ and bicarbonate (Zegeye et al., 2012), but the fate of this GR is not known. Although carbonate GR has been proposed as a precursor to other diagenetic mineral phases in banded iron formations (Halevy et al., 2017), its transformation to these phases has not been observed in nature. Prior studies suggested that iron phases in Lake Towuti sediments undergo dissolution during reductive diagenesis, with secondary growth of diagenetic phases such as magnetite and siderite (Tamuntuan et al., 2015). However, siderite was not explicitly documented in that study, nor is it clear where in the lake and sediment these minerals form.

We discovered spar-sized aggregates (>50 μm) of diagenetic siderite crystals in Lake Towuti sediments, and used detailed geochemical and mineralogical information to describe their features and infer pathways of formation. We suggest that this siderite forms during diagenesis through growth on preexisting primary
phases, including siderite and possibly carbonate GR. We hypothesize that the chemical and mineralogical features of these siderites, and their irregular distribution down core, reflect changes in redox conditions in the pore water and sediment over time, including non-steady-state diagenesis, which likely results from variability in the burial fluxes of ferric iron and organic matter.

METHODS

Sediments were recovered using the International Continental Scientific Drilling Program Deep Lakes Drilling System (https://www.icdp-online.org). Cores from the 113-m-deep TDP-TOW15-1A hole (https://csdco.umn.edu/project/lake-towuti-drilling-project-tdp), drilled in 156 m water depth, were split and imaged at the Limnological Research Center LacCore Facility, Minneapolis, Minnesota, USA. This core mainly consists of alternating green and red clays, the latter containing variably distributed siderite concentrations (Russell et al., 2016). Sedimentary organic matter is mainly autochthonous, albeit at low concentrations, with some contribution of fluvially derived material (Hasberg et al., 2019; Morlock et al., 2019).

Here we focus on material recovered from core catchers. In the field, core catchers were packed into gas-tight aluminum foil bags flushed with nitrogen gas and heat-sealed to keep them under anoxic conditions until mineral extraction. Pore water was retrieved on site using hydraulic squeezers. Alkalinity, pH, and Fe2+ concentrations were determined in the field via colorimetric titration, potentiometry, and spectrophotometry, respectively. Major ions were analyzed at GFZ Potsdam by ion chromatography. Dissolved inorganic carbon (DIC) was calculated from pH and alkalinity. Siderite crystals were retrieved via density separation and sorted by placing a neodymium magnet under the beaker and rinsing out the non-magnetic fraction with deionized water. Siderite imaging and elemental analysis were performed on a Zeiss Ultra 55 Plus field emission scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX). Electron-transparent foils were prepared with a FEI focused ion beam, imaged and analyzed on a FEI Tecnai G2 F20 X-Twin transmission electron microscope (TEM). Structural information was obtained via selected area electron diffraction (SAED) patterns or calculated from high-resolution lattice fringe images (HR-TEM). Freeze-dried powdered bulk sediments and siderite extracts were analyzed in glycerol using a PANalytical Empyrean X-ray diffractometer in a theta-theta configuration. A complete description of all methods is available in the GSA Data Repository1.

1GSA Data Repository item 2019201, Complete description of all methods: Table DR1: Calculated d-spacing and assignments for mineral diffraction patterns; Table DR2: Modeled saturation indices; Figure DR1: SEM images and EDX points of analysis; Figure DR2: TEM images, SAED patterns and interatomic distances for siderite, magnetite, and green rust; Figure DR3: TEM images, EDX points of analysis and SAED patterns for siderite inclusions; Figure DR4: EDX elemental mapping of thin sections; Figure DR5: SEM images of magnetite extracts, is available online at http://www.geosociety.org/datarepository/2019/, or on request from editing@geosociety.org.
DIAGENETIC SIDERITES

We identified many discrete siderite-rich layers in the sediment during our initial core description (Russell et al., 2016). TEM imaging and associated diffraction patterns demonstrate that the extracted crystals are indeed siderite (Fig. 1 top). These analyses also identified minor quantities of carbonate GR and magnetite within siderite crystals at 6.2 m sediment depth (Fig. 1, bottom; Table DR1 in the Data Repository).

Our detailed mineralogical analyses show that the siderites are highly ordered, and we did not detect the amorphous carbonate precursors of siderite that are commonly observed in laboratory experiments (Sel et al., 2012; Dideriksen et al., 2015).

SEM imaging and EDX elemental analysis reveal that siderites develop from initial micritic phases into mosaic crystals (Fig. 2A; Fig. DR1) in the upper 10 m of the sediment, which encompasses ~50 k.y. of depositional history (Costa et al., 2015). Sediment pore waters are saturated with respect to siderite (Table 1), and we therefore infer that siderite forms and grows during diagenesis and burial (Figs. 1 and 2A; Figs. DR1 and DR3). Under these saturated conditions, siderite growth proceeds through twinning and aggregation (Fig. 2A; Fig. DR1), merging microparticulated precursor crystals (>20 μM) into larger spar mosaic-type crystals (>60 μM), and further into bundles and spheroidal clusters (Fig. 2A). For instance, the siderites observed at 82.6 m depth indicate the complete merger of former crystals with growth structures that connect them into a fully ordered single mosaic crystal (Fig. 1D, top), as evidenced by the SAED pattern of the entire crystal, which displays a single crystallographic orientation (Fig. 1, top; Fig. DR2). These deeper siderites, found as bundles of twins and spheroidal aggregates in the sediment (Fig. 2A; Fig. DR1), appear to be dense and have little remaining pore space (Fig. 1F, top; Fig. DR3). In contrast, siderites at 6 m depth are porous and form multiple twins (Figs. 1 [bottom] and 2A; Fig. DR1). Diagenetic maturation thus results in an increasing crystallinity of siderites, which is supported by the greater sharpness of siderite reflections in XRD spectra for deeper siderites (Fig. 2D). We also observe aggregates of nanomagnetite in Lake Towuti in shallow sediments (Fig. DR5) or trapped in siderites (Fig. 1). Those found in magnetic separates of deeper samples may derive from multiple origins (e.g., detrital, volcanic, or authigenic) and some display clear features of dissolution (Fig. DR5). Given their uncertain origins, we do not discuss them further.

| TABLE 1. MODELED SATURATION INDICES |
|-------------------------------------|
| 5 m depth | Saturation 35 m depth | Saturation |
|----------|------------------------|-----------|
| talc      | 1.43                   | siderite  | 1.00 |
| siderite  | 1.29                   | quartz    | 0.71 |
| quartz    | 0.71                   | vivianite | -0.04 |
| vivianite | -0.45                  | calcite   | -0.83 |
| calcite   | -0.68                  | aragonite | -0.97 |
| aragonite | -0.77                  | dolomite  | -1.27 |

Note: Saturation indices based on pH, alkalinity, pore water concentrations of major ions, and borehole temperatures. Bold type—siderite is the only carbonate to be saturated throughout the sedimentary sequence.
With limited sulfate reduction in Lake Towuti, the marine Fe³⁺ concentration (<20 μM) (Vuillemín et al., 2016), microbial Fe³⁺ reduction is likely to promote formation of mixed-valence iron oxides, like carbonate GR and magnetite, as found in nearby Lake Matano (Zegeye et al., 2012), with almost no formation of sulfide minerals. The presence of carbonate GR and nano-magnetite aggregates in siderite pore spaces is evident from HR-TEM images of crystal lattice fringes (Fig. 1, bottom; Fig. DR2). We suggest that the carbonate GR and magnetite form in the upper reaches of the sediments or bottom water and become trapped in siderite interstices during its initial formation (Bell et al., 1987). Chemical micro-niches, such as the pore spaces within siderite, are known to preserve redox-sensitive minerals on geological time scales (Matamoros-Veloza et al., 2018), and trapping in siderite could preserve and shield these mineral grains preventing their further reaction with pore fluids during burial. Fabrics observed in lattice fringes may further suggest epitaxial growth of siderite on carbonate GR (Fig. 1, bottom; Figs. DR2 and DR3), implying that GR may serve as a precursor phase for siderite formation as found in laboratory experiments (Haley et al., 2017). If the GR we see in siderite interstices is indeed primary, its preservation at ~6 m sediment depth implies GR stability over 30 k.y., based on existing constraints on sedimentation rates (Costa et al., 2015). This stands in contrast to carbonate GR instability in laboratory experiments, even at hourly time scales (Ruby et al., 2010; Guilbaud et al., 2013; Haley et al., 2017). GR is known to rapidly convert into an amorphous ferric oxyhydroxycarbonate under standard conditions, or to more stable phases such as goethite and lepidocrocite (Legrand et al., 2004). Alternatively, carbonate GR could form through reaction with oxygen during sample exposure to the atmosphere (Tamaura et al., 1984). We acknowledge that both scenarios are possible.

Elemental mapping of siderite crystals revealed Mn/Fe zonation (Fig. 2B; Fig. DR4), with elevated Mn concentrations at the center of all crystals. We also observed minor substitution of Fe²⁺ by Ca²⁺ (<20%) at the crystal rims. DIC concentrations gradually increase with depth in Lake Towuti’s sediments, likely due to diagenetic organic matter degradation (Vuillemín et al., 2018), which at pH between 7.1 and 7.5 leads to an accumulation of DIC, mainly in the form of HCO₃⁻ (Fig. 2C). The Mn/Fe zonation could thus imply precipitation of siderite in the upper reaches of the sediment where pore water Mn⁴⁺ can accumulate due to reductive dissolution of Mn (oxyhydr)oxides at relatively low HCO₃⁻ activities. High Mg²⁺ concentrations (Fig. 2C) may further inhibit the initial nucleation of carbonates and result in increased substitution of Fe by Mn in siderite grains (Fig. 2B; Fig. DR4).

SIDERITES IN THE PRECAMBRIAN

The morphologies and microchemistry of siderites in Lake Towuti can be compared to siderites from Precambrian rocks to inform on depositional conditions. In Precambrian rocks, pelagic siderites are usually identified as spheroidal crystals that are thought to represent primary precipitates that formed in the water column in response to Fe³⁺ reduction and organic matter oxidation (Condra et al., 2005). These crystals can further transform into rhombohedral and massive siderite in the sediment (Köhler et al., 2013), often with Mg-Ca substitution (Mozył, 1989; Klein, 2005). Fe reduction in the sediment can also lead to formation of similar spheroidal siderite concretions during diagenesis, which can further coalesce into laterally extensive bands of cemented spherules (Coleman, 1993).

In Lake Towuti, we observe laterally continuous siderite-rich layers and the development of continuous agglomerates of mosaic siderite crystals during burial, but with Ca rather than Mg overgrowth, which instead is often associated with marine or diagenetic fluids (Klein, 2005). In comparison, siderite in marine settings usually displays extensive Mg substitution (Mozył, 1989), as observed in Precambrian rocks. The Mn/Fe and Ca concentrations observed in Lake Towuti (Fig. 2B) are typical of siderites formed in freshwater depositional environments (Mortimer et al., 1997), and the main carbonates forming in modern marine pore waters (i.e., calcite, aragonite, dolomite) were all under-saturated in Lake Towuti (Table 1) due to the much lower Ca and Mg ion activities in Lake Towuti pore waters (Fig. 2C) than in seawater.

Spheroidal siderite is often inferred to be a water-column precipitate and precursor for rhombohedral and cemented diagenetic siderites in Precambrian rocks (Konhauser et al., 2005; Köhler et al., 2013). In contrast, the preservation of residual phases trapped in spheroidal mosaic siderite crystals in Lake Towuti may, if primary, suggest initial formation of GR, which is subsequently transformed into siderite in the sediment. We suggest that identification of microchemical zoning in ancient siderites, such as we observe in Lake Towuti siderites (Fig. 3), may provide clearer insight into water-column and pore-fluid chemistries at the time of IFs deposition. For example, the Mn-rich nuclei of siderite crystals preserved in Lake Towuti sediments likely reflects diagenetic Mn reduction, and if identified in IFs, siderites may signal contemporaneous pelagic or sedimentary Mn cycling with corresponding implications for evolving seawater chemistry and the redox state of the ocean-atmosphere system. Likewise, the possible preservation of mineral inclusions in siderite, like the magnetites and possibly GR we see in Lake Towuti, may assist in reconstruction of diagenetic sequences in IFs. Further exploration of IF mineral microchemistry and mineral inclusions, along with corresponding analyses in modern analogues, holds promise for reconstructing environmental conditions at the time of IF deposition.

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