



Carbon- and oxygen-stable isotopic signatures of methanogenesis, temperature, and water column stratification in Holocene siderite varves



Chad Wittkop^{a,*}, Jane Teranes^b, Brady Lubenow^{a,d}, Walter E. Dean^c

^a Department of Chemistry and Geology, Minnesota State University, Mankato, MN 56001, United States

^b Scripps Institution of Oceanography, UCSD, 9500 Gilman Drive, La Jolla, CA 92093, United States

^c US Geological Survey, Federal Center, Denver, CO 80225, United States

^d Department of Geological Sciences, University of Idaho, Moscow, ID 83843, United States

ARTICLE INFO

Article history:

Received 4 April 2014

Received in revised form 24 September 2014

Accepted 25 September 2014

Available online 1 November 2014

Editor: Michael E. Böttcher

Keywords:

Lacustrine

Siderite

Varves

Stable isotopes

Iron formation

Ferruginous lake

ABSTRACT

Manganoan siderite ($[\text{Fe,Mn}]\text{CO}_3$) occurs in abundance of up to 19% (dry weight) as the sole endogenic carbonate within a succession of Holocene, organic-rich, varved sediments from freshwater Otter Lake (OL), Michigan. Radiocarbon dating and varve counts from a 7-m piston core constrain periods of major siderite accumulation to sediments older than 1200 cal yr BP. Sediment petrography suggests that siderite was a seasonal precipitate confined to the summer layer of the varve couplet. Bulk-sediment chemistry reveals cycles in abundance of manganese and aluminum coincident with centennial-scale cycles of siderite accumulation. Siderite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are enriched when the mineral is abundant and depleted when it is least abundant. Samples with high abundance of siderite precipitated in oxygen isotopic equilibrium with modern lake water, but are $\delta^{13}\text{C}$ enriched relative to modern waters. Samples from intervals of low siderite abundance are $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ depleted relative to equilibrium with modern lake water. These data suggest that abundant siderite precipitation occurred when the OL water column was ferruginous (iron meromictic), allowing for enhanced ferrous iron concentrations and dissolved inorganic carbon (DIC) enriched in $\delta^{13}\text{C}$ below the chemocline, where methanogenesis in waters and sediments influenced DIC composition. Seasonal siderite precipitation was triggered by water column alkalinity fluctuations driven by summer calcite dissolution. Manganese substitution in siderite lowered kinetic barriers to low-temperature mineral precipitation. Climate changes and basin filling influenced lake stratification and the rate of siderite precipitation. The siderite occurrence reported here displays remarkable similarity to its occurrence in Paleogene maar lake deposits, suggesting that further studies of Holocene lacustrine siderites may provide insight into ancient sedimentary systems and environments.

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1. Introduction

Sedimentary siderite (FeCO_3) is associated with biological activity from the Archean to present (Tice and Lowe, 2004; Sánchez-Román et al., 2014), and requires anoxic waters, elevated $p\text{CO}_2$, and low sulfur to accumulate (Bernier, 1981; Mozley, 1989; Romanek et al., 2009). It is known in Holocene lacustrine sediments (e.g. Anthony, 1977; Talbot and Kelts, 1986; Crausbay et al., 2006), but its genesis in this environment is understudied. Two precipitation pathways have been considered in modern lakes: anaerobic porewater (Emerson, 1976), or in a chemically stratified water column (Anthony, 1977). Subsequent porewater (Postma, 1982) and limnochemical studies (Sigurdsson et al., 1987) provided support for both pathways. Diagenetic siderites are more widely reported, but a handful of studies provide evidence that water-column precipitation occurs in some circumstances

(Bahrig, 1988; Rajan et al., 1996). Given the diversity of modern lacustrine environments, multiple precipitation pathways may be possible, but the potential for water-column precipitation of siderite is particularly noteworthy and understudied.

The growing importance of siderite to investigations as diverse as Archean biogeochemical cycling (Ohmoto et al., 2004; Fischer et al., 2009) and Phanerozoic climate reconstruction (Ludvigson et al., 1998) will place increasing emphasis on the interpretation of stable isotopes in this mineral, requiring continued efforts to constrain mineral genesis in the laboratory and in modern analogs. Recent documentation of lacustrine Mg-Fe-bearing clays and carbonates on Mars (Michalski et al., 2013) provides further motivation for these studies. Laboratory synthesis of siderite has not been successful below 10 °C (Zhang et al., 2001), limiting the confidence of oxygen stable isotope interpretations at low temperatures (Mortimer and Coleman, 1997; Zhang et al., 2001; Fernandez et al., 2014). Since low-temperature precipitation may dominate in environments from the Archean to Mars, further studies are needed to advance our understanding of siderite precipitation and stable isotopic behavior in these conditions.

* Corresponding author. Tel.: +1 507 389 6929.

E-mail address: chad.wittkop@mnsu.edu (C. Wittkop).

Ferruginous lakes offer an analog environment where these problems can be explored. These lakes (described as iron-meromictic or iron-stratified in earlier studies) are low-sulfate, permanently stratified (meromictic) systems enriched in dissolved iron in their deep waters (Crowe et al., 2008). Studies of these unusual systems have provided insight into biogeochemical cycling of nutrients and metals (Michard et al., 1994; Taillefert et al., 2002; Crowe et al., 2011; Busigny et al., 2014). Initial reports of siderite in lake sediments came from ferruginous systems (Anthony, 1977; Sigurdsson et al., 1987), and given their utility in serving as Archean ocean analogs (Crowe et al., 2008), additional study of chemical sedimentary processes in these rare systems promises to advance our understanding of siderite genesis in ancient environments.

In this contribution we document a new siderite occurrence from the Holocene sediments of Otter Lake, Michigan, USA (OL). This occurrence is noteworthy for the presence of abundant (up to 19 wt%), primary siderite in millimeter-scale varves. These seasonally laminated sediments provide chronologic control, and their delicate texture offers petrologic constraint on mineral genesis. And in contrast to many mixed carbonate systems, siderite is the only major endogenic phase present in OL sediments, allowing for more constrained interpretation of paleoenvironmental influences on mineral genesis and stable isotopic composition. Although the lake is not ferruginous today, we present geochemical evidence that it experienced several significant periods of ferruginous sedimentation in the late Holocene. The consistently low temperature of deep lake water in this setting also provides an opportunity for testing hypotheses regarding the temperature control on mineral precipitation and stable isotopic composition.

The relative abundance of siderite, its carbon- and oxygen-stable isotopic composition, and the geochemistry of lake water and sediments are used to constrain the environment of OL siderite precipitation. Our data will demonstrate that OL siderite most likely represents a low-temperature, primary water-column or lake-floor precipitate in oxygen isotopic equilibrium with lake water. As such, this system may provide important context for distinguishing low-temperature siderites

precipitated from permanently stratified water bodies in modern and ancient environments.

2. Materials and methods

OL is an ice-block (kettle) basin located in a late-Pleistocene glaciofluvial and diamicton complex in east-central lower Michigan (43°13'9.48" N lat., 83°27'30" W long; Farrand and Bell, 1982; Fig. 1). Pleistocene sediments are in part derived from local Paleozoic shales and carbonates, which include black shales of the Mississippian Michigan Formation that underlie the site (Milstein, 1987).

The lake has a surface area of 27.5 ha and a maximum depth of 35.6 m. A sill at a maximum depth of 3 m further separates the lake into two sub-basins. Lake watershed area is 335.6 ha, and the primary lake inlet collects surface water from chain of small ponds surrounded by wetlands, which comprise nearly 28% of the watershed. A small outlet flows from the south end of OL.

A 7-m Kullenberg piston core was raised from the deepest point in the lake in July 1999 using a raft system modified from the design of Kelts et al. (1986). This core is archived at the National Lacustrine Core Repository (LacCore), University of Minnesota, and all lithological analyses of it were performed there unless otherwise noted. The core was split, photographed, and logged in terms of macroscopic texture and structure. Bulk-sediment and lamination composition was analyzed in smear slides using a petrographic microscope. Portions of core were embedded with Spurr's resin using both acetone-replacement and flash-freeze freeze-dry techniques, and cured for thin section preparation (Lamoureux, 1994; Lotter and Lemcke, 1999). Littoral sediment samples were hand collected in March 2012.

Water samples were collected using a VanDorn non-metallic sampler at indicated intervals and filtered through a 0.2 μm nylon filter. Carbon isotope samples were filtered into glass serum vials with no headspace and preserved with CuCl₂. Samples for oxygen isotope analyses were filtered into glass scintillation vials. All samples were stored in a cooler in the field and refrigerated in the laboratory prior to analysis.

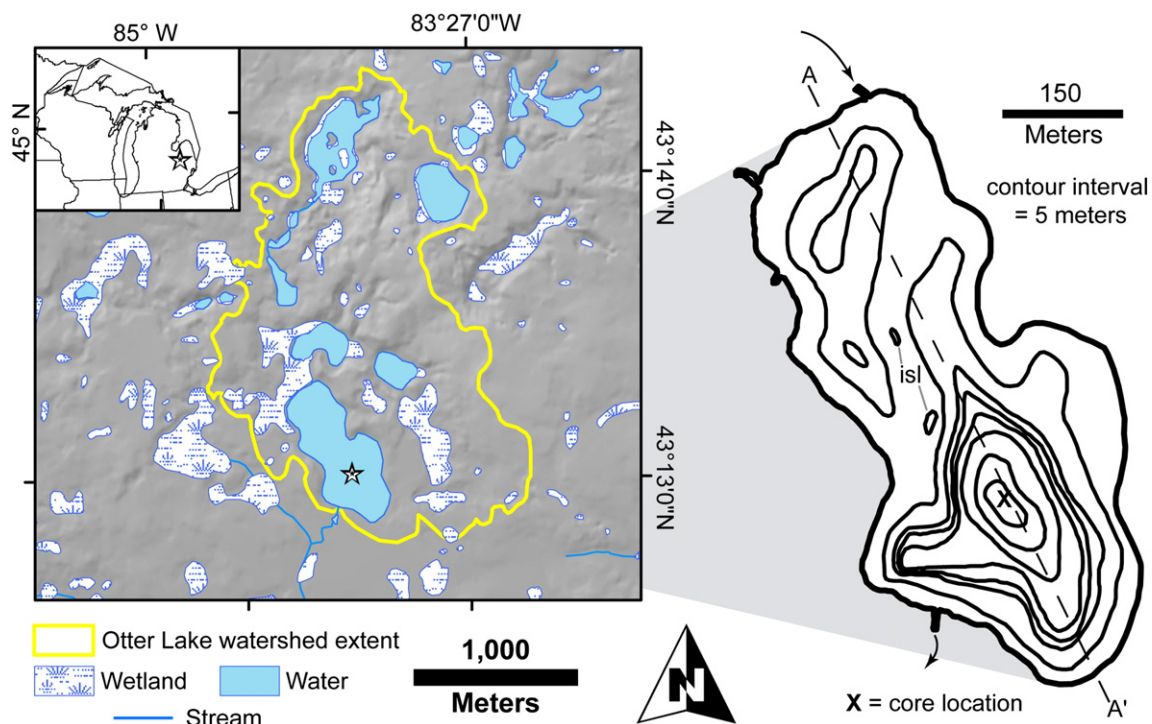


Fig. 1. Location and bathymetry of Otter Lake (piston core location indicated by star, isl = islands). Bathymetric contours after Michigan Department of Conservation (1963). Line A–A' was used to construct lake cross sections in Fig. 7.

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