Quaternary International xxx (2017) 1–13

Contents lists available at ScienceDirect

Quaternary International

journal homepage: www.elsevier.com/locate/quaint

Evaluating abiotic and microbial factors on carbonate precipitation in Lake Acig-ol, a hypersaline lake in Southwestern Turkey

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ARTICLE INFO

Article history:
Received 12 September 2017
Received in revised form
19 December 2017
Accepted 26 December 2017
Available online xxx

Keywords:
Lake Acıgöl
Hypersaline
Carbonates
Microbial processes
Isotopes

ABSTRACT

The recent carbonate precipitation occurs in Lake Acıgöl, a hypersaline playa lake. Elucidating precipitation mechanisms of carbonate minerals under particularly supersaturated ionic solution at low temperature may hold key understanding to recognize microbial fingerprints throughout the Earth history. In the presented study abiotic and microbial factors controlling carbonate precipitation mechanisms are investigated by using geochemical, isotopic and chemical approaches. Our data demonstrated that aragonite, calcite and dolomite are readily precipitated in oxic column of lake water in decreasing order. Major metabolites profile of pore water showed that carbonate alkalinity and pH increased by microbial activity seems to be insignificant in the lake sediments to support precipitation. On the contrary a positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values of carbonates suggest that carbonate super-saturation occurs as a result of evaporation and associated degassing of CO_2in the lake basin. However, a putative microbial role such as binding of cations to microbial cell wall or EPS to overcome kinetic inhibitors (e.g Mg^{2+}) is likely possible in the lake as a driving carbonate precipitation mechanism. Overall, the present study demonstrated that carbonate precipitation in the lake is the result of complex players, such as lake water chemistry, ionic interactions, evaporation and EPS-organic compounds (e.g EPS) in addition to kinetic microbial processes. The data also provide a fundamental insight which is that revealing of changes in carbonate mineralogy of the lake, strongly influenced by evaporation, would provide significant insights about paleoclimatic conditions of the region.

1. Introduction

Carbon cycle is intimately linked with the other major geochemical cycles such as S, N and P in marine and non-marine settings. The formation of carbonate minerals in geochemically diverse settings can be very complex involving evaporation, dissolution-re-precipitation, degassing of CO_2 in addition to microbial processes (Thompson and Ferris, 1990; Thompson et al., 1997; Warthmann et al., 2000; Wright and Oren, 2005; Forti, 2005; Balci, 2010; Meister et al., 2011a, 2011b; 2013; Kaplan et al., 2013; Balci et al., 2016; Balci and Demirel, 2016; Eren et al., 2016). Elucidating of carbonate precipitation mechanism has been a subject of numerous research for the last few decades with a special interest to microbial processes (Castanier et al., 1999; Van Lith et al., 2003, Braissant et al., 2003; Sánchez-Román et al., 2009, 2011; Bontognali et al., 2010). Such processes profoundly contributed to carbonate production throughout the Earth's history (Grotzinger and Knoll, 1999; Thompson et al., 1997; Reid et al., 2000) In particular, demonstration of dolomite precipitation with microbial culture, kinetically inhibited at low temperature, has brought new interpretations for carbonate formation environments (Friedman and Sanders, 1967; Kenward et al., 2009; Krause et al., 2012). Later on experiments carried with different microbial species, particularly with sulfate reducing bacteria (SRB), suggest a microbial factor involved in carbonate precipitation, particularly dolomite (Roberts et al., 2004; Vasconcelos and McKenzie, 1997; Vasconcelos et al., 1995).

Numerous laboratory and field studies has been carried out to elucidate the role of microorganisms in the precipitation of

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https://doi.org/10.1016/j.quaint.2017.12.046
1040-6182/

carbonates (Ferrer et al., 1988; Castanier et al., 1999; Rivadeneyra et al., 1997, 1998, 2004; Van Lith et al., 2003; Sánchez-Román et al., 2009, 2011). It is now broadly accepted that a wide range of microbial group such as methanogens, sulfur oxidizing bacteria, halophilic bacteria and cyanobacteria are involved in carbonate precipitation in various natural environments. One of the most fascinating environment among them is hypersaline lakes where extreme chemical conditions (e.g pH, salt) are dominant. Despite this less favorable life conditions, high rate of primary production measured in these environments indicated that salt adapted microorganisms are in fact active under even this harsh conditions (Oren, 2002: Yanhe Ma et al., 2010). Now, it is known that hypersaline environments are far from sterile and have unique and diverse microbial populations (Yanhe Ma et al., 2010; Balci et al., 2016). For example, cyanobacteria and bacteria are known to involve in carbonate precipitation in hypersaline environments and several carbonate precipitation mechanisms have been proposed (Sánchez-Román et al., 2009, 2011; Balci et al., 2016).

Bacteria/archea can induce the precipitation of carbonates either modifying the conditions of their surrounding environments as a results of by products of their metabolism and thus concentrate ions in the cell wall or/and acting as nucleation sites by adsorbing Ca^{+2}, Mg^{+2} and other metallic cations onto their cell wall and/or extracellular polymeric substances (EPS) (Rivadeneyra et al., 2006). Various moderately halophilic bacteria were tested for their capacity for carbonate precipitation in various studies (Rivadeneyra et al., 2006, 2004, 2000, 1998, 1993). The results of many researches indicate that microorganisms are able to precipitate a wide range of carbonate minerals at low temperatures and they are important players in modern environments, as well as in the geologic records. Nevertheless; our knowledge about the microbial effect on nucleation and growth of carbonates at molecular level is still missing. It is still under debate if mineralization occur due to side effect of metabolism (biologically induced) or an intentional effect of microorganism to benefit from their environment. A better understanding of abiotic and microbial processes during carbonate precipitation in various geological settings, particularly in hypersaline conditions, may provide crucial information about interactions between biosphere and atmosphere in modern and geological past as well as search for life in extraterrestrial environments. Authigenic carbonates from hypersaline environments often show metastable polymorphs with a range of euhedral to spheroidal crystal habits and the physico-chemical conditions cause such crystal shapes remain poorly described. Locating in Southwestern Turkey, Acigöl with extreme water chemistry (e.g high salinity, superionic) may provide such opportunity to fully investigate the influence of microbial vs abiotic processes on carbonate precipitation as well as crystal chemistry habits under extreme conditions besides providing opportunity to look if biologically originated carbonate minerals in fact carry their biogenicity. Lake Acigöl basin and its vicinity has been a subject of various researches including mineralogy, hydrogeochemistry, geochemistry, geology (Akbul and Kadir, 2003). However, there have been a few study focusing on carbonate precipitation mechanisms, particularly from biotic side. In a recent study Balci et al., 2016, and Menekse et al., 2011 were isolated halophilic cultures from the lake sediments to test their capacity to precipitate authigenic carbonate minerals in the laboratory mimicking the lake conditions. Although the authors revealed possible biological influences on carbonate precipitation as suggested by Mutlu et al., 1999, the study to investigate if mineralogical, isotopic and geochemical features of Lake's sediments along with the pore and surface water in fact reflect precipitation mechanisms of carbonates (biological and/or abiotic) is still lacking. In fact, the exact role of microorganisms is still poorly constrained during authigenic carbonate formation in the lake.

In this study, for the first time a combined geochemical approach was used in order to evaluate microbial vs. abiotic processes on recent carbonate precipitation in hypersaline playa Lake Acigöl. For this purpose, the mineralogy of surface and core sediments, chemical composition of pore water, C and O isotope compositions of bulk sediment of two coring sites, located in north and south shore of the lake, were comprised with chemical, O and H isotope composition of lake water, groundwater and spring water. These results were then used to calculate saturation state of various carbonate minerals (e.g aragonite, dolomite, calcite) in pore water, lake, spring and groundwater to independently elucidate abiotic factors from microbial factors. Microbial factors on carbonate precipitation were evaluated based on metabolites (HS^-, NH_4^+, NO_3^{2-}) obtained from pore water, morphology of carbonates and C and O isotope composition of bulk carbonate sediments.

1.1. Description of the study site

Lake Acigöl, a shallow hypersaline lake, is located SW of Turkey at an elevation of 836 m above sea level and has a surface area about 60 km^2 with a reported maximum depth of <2 m (in the central part) (Fig. 1.) (Helvacı et al., 2012). The Acigöl basin is a closed drainage basin where a semiarid continental climate dominates. The Lake's drainage basin is approximately 1292,0 km^2 and the total annual precipitation in the coasts of lake is 368–392 mm (2008) and the water depth and coverage of water in the lake vary seasonally. Water depth, increases from north to south where the highlands are located and the north of the lake is generally inundated throughout the year. Except southeastern margin of the lake, ephemeral dry mud flats comprise most of the lake area throughout the year and dry mud flats, particularly in the northern part of the lake, transitionally passes into brine soak sediments often covered with a few cm halite. The Lake Acigöl brines are predominantly $Na-CI-SO_4$ type. Springs and groundwater are the main inflow source of water to the lake.

The south of the lake comprises cherty limestone aged in Jurassic –Cretaceous and cretaceous aged ophiolites consisting of dunite, harzburgite, and gabbroic rocks with limestone-chert and radiolarite blocks (Helvacı et al., 2012; Alçiçek et al., 2005; Mutlu et al., 1999). The north of the lake covering the flat area composed of alternation of conglomerate, sandstone and mudstone. Quaternary alluvium deposits consisting of fluvial and lacustrine sediments are the youngest sediments around the lake.

2. Materials and methods

2.1. Field samplings

Field sampling was conducted in April 2013 and July 2015. Water samples were collected from lake (n = 7, LW), spring (n = 3, SW) and groundwater (well water) (n = 2, GW) (Fig. 1). Upon collection and filtration (Sartorious 0.2 µm syringe filter) 100 ml water sample was divided into two part: trace grade nitric acid added 50 ml for metal analysis and the rest was used for major ion analysis. For alkalinity measurements 50 ml filtered water was collected into polyethylene bottle, no headspace was left in the bottles, and bottles were kept upside down until analysis.

Physicochemical characteristics of all the water samples such as pH, temperature, EC and salinity were measured in-situ with pH and conductivity probes (WTW). Additional water samples were collected for isotope measurements ($\delta^{18}O$ and δ^2H). Anion, cation and metal compositions of all the water samples were analyzed by atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) at Mersin University Sciences

Please cite this article in press as: Balci, N., et al., Evaluating abiotic and microbial factors on carbonate precipitation in Lake Acig-ol, a hypersaline lake in Southwestern Turkey, Quaternary International (2017), https://doi.org/10.1016/j.quaint.2017.12.046