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Geochemistry of recent aragonite-rich sediments in Mediterranean karstic marine lakes: Trace elements as pollution and palaeoredox proxies and indicators of authigenic mineral formation

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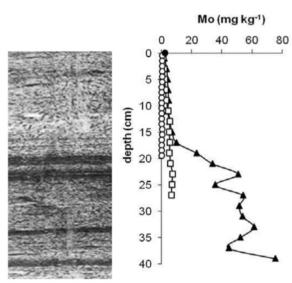
HIGHLIGHTS

- Sr was used as a proxy indicating authigenic formation of aragonite in marine sediments.
- Distribution of Mo, Tl, U and Cd indicate changes in redox conditions in core sediments.
- Mo, Tl, U and Cd are associated early formed nanostructured authigenic framboidal pyrite.
- Concentration of Zn, Cu, Pb, Sn and Bi in core sediments indicates a low level of pollution.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the geochemical characteristics of recent shallow-water aragonite-rich sediments from the karstic marine lakes located in the pristine environment on the island of Mljet (Adriatic Sea). Different trace elements were used as authigenic mineral formation, palaeoredox and pollution indicators. The distribution and the historical record of trace elements deposition mostly depended on the sedimentological processes associated with the formation of aragonite, early diagenetic processes governed by the prevailing physico-chemical conditions and on the recent anthropogenic activity. This study demonstrated that Sr could be used as a proxy indicating authigenic formation of aragonite in a marine carbonate sedimentological environment. Distribution of the redox sensitive elements Mo, Tl, U and Cd was used to identify changes in redox conditions in the investigated lake system and to determine the geochemical cycle of these elements through environmental changes over the last 100 years. The significant enrichment of these elements and the presence of early formed nanostructured authigenic framboidal pyrite in laminated deeper parts of sediment in Malo Jezero, indicate sporadic events of oxygen-depleted euxinic conditions in the recent past. Concentrations of trace elements were in the range characteristic for non-contaminated marine carbonates. However, the increase in the concentrations of Zn, Cu, Pb, Sn, Bi in the upper-most sediment strata of Veliko Jezero indicates a low level of trace element pollution, resulting from anthropogenic inputs over the last 40 years. The presence of butyltin compounds (BuTs) in the surface sediment of Veliko Jezero additionally indicates the anthropogenic influence in the recent past.

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1. Introduction

The geochemical processes occurring in recent marine sediments govern the regional and the global cycling of a variety of inorganic and organic compounds, particularly trace elements. Literature abounds with studies on the trace element distribution in sediments of different marine sedimentary environments with respect to their deposition, distribution, association, diagenesis, mobilization, and historical record of their accumulation (Dolenec et al., 1998; Singh, 2009; Morelli et al., 2012; Kalantzi et al., 2013; Jurina et al., 2015; Kalnejais et al., 2015). During the last decade, a new approach that is based on the use of trace elements as proxies for determination of the seawater chemistry and changes in physico-chemical conditions in marine and lacustrine sedimentological systems was applied in geochemistry (Elbaz-Poulichet et al., 2005; Tribovillard et al., 2006; Large et al., 2014). It has been reported that redox sensitive elements, particularly Mo, Cd, U and V could be used as proxies in determination of redox conditions in different recent and palaeo-depositional environments (Calvert and Pedersen, 1993; Tribovillard et al., 2006). While the chemical mechanisms of their scavenging in natural sulfide-rich and oxygen-deficient environments are not entirely understood, it is assumed that these are concentrated in early formed pyrite mineral phase (Elbaz-Poulichet et al., 2005; Chappaz et al., 2014). Recently, Large et al. (2014) have shown that trace element content of sedimentary pyrite can be used as a new proxy for the so-called "deep-time ocean-atmosphere evolution". Employing the trace elements as palaeoredox indicators is not possible in sedimentological environments where anthropogenic activity overprints naturally occurring geochemical markers (Dolor et al., 2012).

Coastal shallow-water marine carbonate settings represent a specific environment where geochemical processes are dependent on the recent carbonate sedimentology, primarily the authigenic formation and deposition of carbonate mineral phases (Sondi and Juračić, 2010). Besides, the variety of physico-chemical and biotic processes, together with terrigenous and anthropogenic load, result in a trace element distribution that reflects specific conditions prevailing during their deposition and early diagenetic processes in marine carbonate sediments (Cuculić et al., 2009). Most previous geochemical studies of modern carbonate sediments were conducted in geographically extensive areas characterized by complex and overlapping environmental influences that do not enable identification of dominant processes of general relevance to their geochemistry. Answers that are more specific may be found in small, well-defined systems, in which the number of interacting factors is significantly reduced and offers a possibility of better understanding of the behaviour and fate of trace elements. Such a natural model system was recognized in the southern Adriatic, in two marine lakes situated on the island of Mljet. These lakes represent a unique, semi-enclosed Mediterranean environment, characterized by authigenic formation of recent fine-grained aragonite sediments formed under temperate climate conditions (Sondi and Juračić, 2010). A small, protected, and well-defined environment of the Mljet Lakes allows correlation between sedimentological and geochemical characteristics and simple tracing of early diagenetic processes and anthropogenic influence on the geochemical cycle of trace elements during the recent past.

Previous studies carried out in this area have provided evidence of remarkable environmental changes and reconstruction of the lake formation during the Holocene (Wunsam et al., 1999), and on the morphometric and general sedimentation characteristics of the Mljet Lakes (Vuletić, 1953). Recently, the role of whiting events, drifting milky clouds of water, in the formation of modern aragonite-rich lake sediments was described (Sondi and Juračić, 2010) and geochemical conditions for their preservation during early diagenesis were determined (Lojen et al., 2010). In addition, Cuculić et al. (2009) attempted to determine natural and anthropogenic sources of trace elements, primarily in the seawater and partially in sediments of the Mljet Lakes and the adjacent coastal environment. However, the distribution and the fate of trace elements in lake sediments was not systematically scrutinized; it was not contemplated in the sense of sedimentation dynamics, mineral composition of sediments and early diagenetic processes that occur in sediments of the lakes.

This paper aims to provide insight into the dominant geochemical processes that govern the cycle of trace elements in modern marine aragonite-rich sediments of the unique semi-enclosed karstic environment of the Mljet Lakes. In particular, it reports on the role of authigenic precipitation of aragonite and pyrite, early diagenetic processes and anthropogenic input on their deposition and distribution in lake sediments. This study endeavors to contribute new evidence on the dispersal and the fate of trace elements and their use as pollution and palaeoredox indicators in this setting. Finally, it registers anthropogenically and diagenetically driven changes in a modern, aragonite-rich Mediterranean sedimentary environment in the recent past.

2. Study area

The Mljet Lakes (Veliko and Malo Jezero) are located in the western part of the island of Mljet (Adriatic Sea) (Fig. 1). The island is built up of Late Mesozoic platform carbonates (Fig. 1, inset). The geological settings and the formation of the lakes was previously described in details (Sondi and Juračić, 2010). Being connected with the open sea, they contain seawater and therefore can be termed marine lakes. The depth of Malo Jezero is 29 m and the depth of Veliko jezero 47 m. At present, the water exchange between the open sea and Veliko and Malo Jezero is driven by tidal currents. Due to the small tidal range and very shallow straits connecting Soline Channel and Veliko Jezero (2.5 m), and Veliko and Malo Jezero (0.6 m), the water exchange is negligible which may cause occasional stratification of the water column throughout the year. However, the occurrence of anoxic/euxinic conditions in the water systems of the Mljet Lakes was not observed during the last decade (Jasprica et al., 1995; Benović et al., 2000). Detailed physico-chemical properties (salinity, temperature, oxygen and pH) of the lake waters were described in previously published papers (Buljan and Špan, 1976; Benović et al., 2000). During the summer, as a result of excessive heating, salinity is increased, particularly in the surface water layer of the Malo Jezero.

3. Sampling and methods

3.1. Sampling

Undisturbed sediment cores up to 50 cm long were collected at Malo Jezero (S1; depth 29 m), Veliko Jezero (S2; depth 44 m), and the open sea (S3; depth 110 m) (Fig. 1), using the Uwitec gravity corer. Immediately after sampling, pH and Eh parameters in separate sediment cores were measured. Prior to analyses the sediment cores were subdivided into 2 cm segments, freeze-dried and kept until further mineralogical and geochemical analyses were performed. In order to extract the pore water from sediments, immediately after sampling sediment cores were transferred to the laboratory and sectioned in a glove box into 2 cm segments under nitrogen atmosphere. These parts were centrifuged at 5000 rpm for 30 min; the pore water was taken into plastic syringe and filtered through 0.45 μm Minisart cellulose acetate (Sartorius) filters in inert nitrogen atmosphere. The obtained samples were placed into HDPE bottles and acidified with HNO_3 (TraceSelect, Fluka). Along