Title:

Climate influence on organic carbon burial efficiency as revealed from a multi-proxy lake sediment record in Croatia

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Key points:

- Sr/Ca of bulk sediment representing the Sr/Ca of inorganic needle-like aragonite is mainly temperature driven with hydrological conditions playing only a subordinate role.
- During the 8.3 to 2.6 cal ka BP time period four major and six minor cold and dry events were recognized.
- Cold and dry climate state enhanced anoxic conditions in the lake water column, which increased organic carbon burial efficiency.

Abstract

The drivers of the efficiency in organic carbon (OC) burial are still poorly understood despite their key role in reliable projections of future climate trends. Here we shed new light on this question by presenting paleoclimate time series including OC content in sediments from Lake Veliko jezero, Croatia. We identified the Sr/Ca ratio in bulk sediments as (comparative) palaeotemperature and palaeohydrology indicator. Four major and six minor cold and dry events were detected in the 8.3 to 2.6 cal ka BP interval. The combined assessment of Sr/Ca ratios, OC content, C/N ratios, $\delta^{13}C$ data, and modelled proxies for palaeoredox conditions and aeolian input reveals that cold and dry climate state promoted anoxic conditions in the lake enhancing preservation of organic matter and leading to increased OC burial efficiency. Our study contributes to that projected future increase of temperature might play an important role in OC burial efficiency of meromictic lakes.

Plain Language Summary

While covering only 2% of the Earth´s surface lakes store disproportionally large amounts of organic carbon, half of the amount stored in the oceans. In this way organic carbon is removed from a short-term carbon cycle for longer (geological) period of time. Despite this fact and the impact of the carbon on climate dynamics, there are questions about the carbon burial in lakes that still remain unaddressed. For example, is the burial efficiency enhanced or suppressed by a temperature increase? Also, what are direct mechanisms responsible for changes in carbon burial efficiency? Although, there is probably no general answer due to the large variety of lakes in nature, here we present results of a study in which high resolution palaeoclimate proxy record based on the strontium to calcium ratio is correlated with indicators for redox conditions and past aeolian input. In this way palaeoenvironmental and palaeoclimate conditions have been reconstructed and compared to organic carbon content of the lake sediments. Our study demonstrates that during colder periods concentrations of organic carbon are higher, which is a direct consequence of a change in redox conditions mediated by redox zone boundary and thermocline depths.

1. Introduction

Lakes, with disproportionally large amounts of buried organic carbon (OC) per year if compared to the oceans (Mendonça et al., 2017), are of great importance for the global carbon budget and cycle and thus might have a vast impact on climate changes also in the future. However, the climate influence on OC burial efficiency is still not precisely understood. Temperature influence on the OC burial efficiency has been studied extensively, mainly for the lakes of higher northern latitudes (Gudasz et al., 2010; Larsen et al., 2011; Anderson et al., 2013; Sobek et al., 2014; Heathcote et al., 2015). Despite extensive efforts as represented by the large number of studies on this topic, there is still no overall supposition on a possible temperature influence on the OC burial efficiency. Nor are the main driving mechanisms recognized, which are likely and directly responsible for the observed changes in OC content of the lake sediments. Some studies infer that higher temperatures are enhancing OC burial mainly as a consequence of a denser vegetation cover (Algesten et al., 2003; Sobek et al., 2003; Sobek et al., 2009; Larsen et al., 2011; Xu et al., 2013), while at the same time an increase in temperature is positively correlated to OC mineralization (Sobek et al., 2009; Gudasz et al., 2010; Gudasz et al., 2015). In more recent studies the anthropogenic influence is preferred, primarily through the role of the reactive nitrogen and phosphorus on OC burial efficiency (Anderson et al., 2013, 2020; Heathcote et al., 2015), and a temperature effect negated. Furthermore, oxygen exposure time and redox conditions in the water may also play a prominent role in the OC burial efficiency (Sobek et al., 2009; Sobek et al., 2014; Carey et al., 2018; Bartosiewicz et al., 2019).

The majority of previous studies of OC burial efficiency were focussed on recent and sub-recent lake sediments, where climate effects can easily be concealed by anthropogenic influence. Additionally, in latitudinal studies the temperature effect can be masked by other variables such as changes in vegetation cover and/or precipitation rate. To infer the climate influence on OC burial efficiency we have studied sediments of Lake Veliko jezero, Croatia (Figure 1) for the period 8.3 to 2.6 cal ka BP. In detail we interpreted the OC content in the context of high-resolution relative palaeoclimate and palaeoredox proxies as well as an indicator for past aeolian activity. During the studied interval Lake Veliko jezero was a brackish, meromictic lake (Wunsam et al., 1999), which is now submerged because of the Holocene sea level rise. Our approach for correlating palaeoclimate and palaeoredox proxies

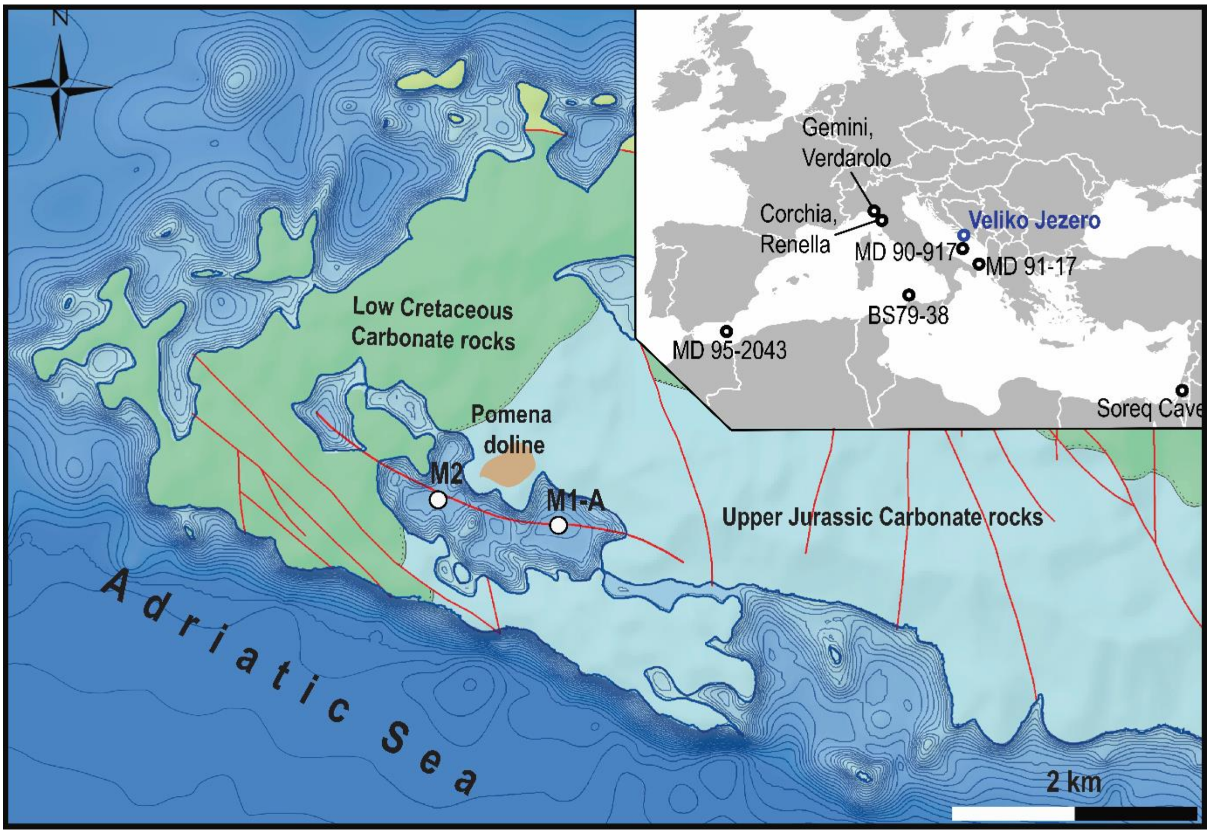

Figure 1. Location of Lake Veliko jezero and Mediterranean climate records as discussed in the text in the upper right corner with the locations of Cores M1-A and M2 and the stratigraphical and lithological surrounding of the Lake Veliko jezero.

was made taking into account compositional nature of the geochemical data (Pawlowsky-Glahn et al., 2015), that enabled more precise interpretations. The Sr/Ca ratios of the bulk sediment mainly derives from Sr and Ca concentrations of needle like aragonite in Core M1-A and was used as a paleoclimate, temperature proxy with higher ratio indicating cooler conditions. We validated the reliability of the data and interpretations by also acquiring the same kind of data for Core M-2 that was taken from a different basin of the same lake. An age-depth model of Core M1-A (Figure 2) is described in Razum et al., (2020a). The significance of Sr/Ca ratio as a palaeotemperature proxy is also confirmed by correlation with other previously published studies including the main Holocene climatic events from the wider Mediterranean region (Cacho et al., 2001; Sangiorgi et al., 2003; Combourieu-Nebout et al., 2013; Siani et al., 2013; Regattieri et al., 2014; Samartin et al., 2017).

2. Results and discussion

Core M1-A recovered from Lake Veliko jezero is 417 cm long, four lithological units were distinguished (Figure 2). The first unit (417 to 343 cm) is a terra rossa type soil, the second unit (343 to 241 cm) is marsh to shallow lake sediment, the third unit (241 to 121 cm) consists of deep lake sediment characterized by alternations of white and dark laminas mainly composed of aragonite and organic matter. The last unit (121 to 0 cm) is made up of gray homogenous marine sediment with a few centimeters of oxidized lake sediment in the lowermost part. The third unit and the oxidized part of the unit four lake sediment were in the focus of this study. Core M2 resembles Core M1-A with the difference that unit boundaries are in different depths. Therefore, the studied interval spans from 127 to 266 cm in this core.

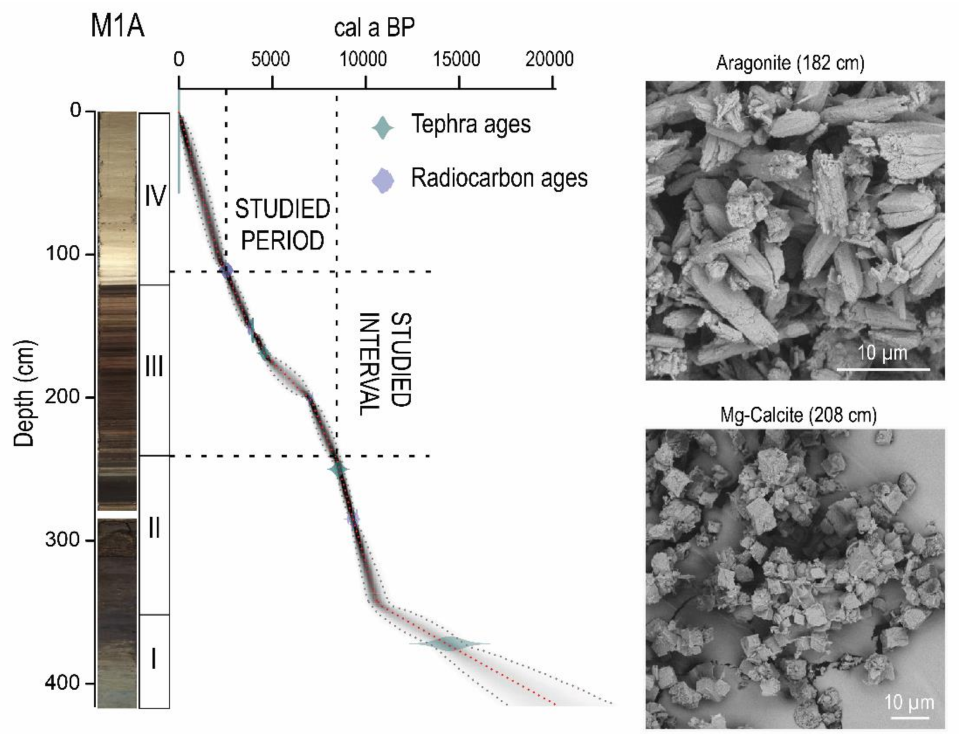

Figure 2. Age-depth model for Core M1-A from Lake Veliko jezero (Razum et al., 2020a), core images and lithological units are shown next to the depth scale. SEM images of inorganic aragonite and Mg-calcite are shown on the right-hand side.

2.1. High-resolution XRF scanning and age-depth model

The Sr/Ca records were obtained by high-resolution XRF core scanning at split core surfaces in 1-cm and 2-mm resolutions. We compared the Sr/Ca data and ratios between the two investigated cores (M1-A and M2) to confirm robustness of our record and to exclude any potential analytical artefacts. The geochronological age of Core M2 is based on one plant remain sample, which was dated by radiocarbon methodology. Additional three datums were included in the age-depth model of this core. Two of these ages are based on visible tephra layers correlated to the known volcanic eruptions previously recognized in Core M1-A (Razum et al., 2020a). The third date corresponds to a time of marine intrusion into the lake, which is marked by a sharp boundary between lithological units three and four (Figure 2) in both cores. It was radiometrically dated in Core M1-A (Razum et al., 2020a). Individual radiocarbon dates were calibrated using the R package rbacon (Blaauw and Christen 2018). Despite lower resolution of the Core M2 record it is evident that major peaks and throughs in Sr/Ca are well presented in both datasets (Figure 3).

2.2. Sr/Ca ratio as palaeoclimate proxy

Our working hypothesis was that the Sr/Ca ratio in bulk sediment almost exclusively reflects the Sr/Ca ratio of needle-like aragonite in the sediment (Figure 2). Needle-like aragonite precipitates nowadays during late spring and summer in adjacent lake Malo jezero (Sondi & Juračić, 2010). Since Sr/Ca ratio of needle-like aragonite is largely temperature dependant (Kinsman & Holland, 1969; Dietzel et al., 2004) we assume that the Sr/Ca ratio of the studied sediment could be used as a relative palaeotemperature proxy. Mineralogical analysis performed with a X-ray diffraction (XRD) and scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS) proved that inorganic needle-like aragonite is the main mineral and nearly the only carbonate phase in our investigated samples (Figure 2). The only exception is an interval from 201 to 214 cm where inorganic rhombohedral Mg-calcite is the main carbonate phase confirming the results of Wunsam et al., (1999). According to the age model of Core M1-A, the occurrence of Mg-calcite coincides with known time intervals of wet climate during which lake levels were high and generally corresponding to pluvial periods observed in the wider Mediterranean region (Figure 3 and 4, from ca. 7.6 to 7 ka BP) (Bar-Matthews et al., 1997; Kallel et al., 1997; Bar-Matthews et al., 1998; Bar-Matthews & Ayalon, 2011; Magny et al., 2012 Combourieu-Nebout et al., 2013; Siani et al., 2013; Zhornyak et al., 2011; Regattieri et al., 2014). We propose that during this period increased freshwater input lowered the Mg/Ca ratio in the lake water leading to the Mg-calcite precipitation and hindering the precipitation of aragonite. This consequently led to Sr/Ca decrease in our records because Mg-Calcite incorporates Sr in the crystal lattice less effectively compared to the aragonite (Kitano et al., 1971) thus the Sr/Ca ratio of bulk sediment cannot be interpreted as a relative palaeotemperature proxy in this interval. However, the predominance of Mg-Calcite over aragonite points to wetter climate conditions which are also observed in the wider region during this time period (Bar-Matthews et al., 1997; Kallel et al., 1997; Bar-Matthews et al., 1998; Bar-Matthews & Ayalon, 2011; Magny et al., 2012 Combourieu-Nebout et al., 2013; Siani et al., 2013; Zhornyak et al., 2011; Regattieri et al., 2014).

In order to be able to utilize the Sr/Ca ratio as a relative paleotemperature proxy we have proven that detrital Sr and Ca input is negligible. XRD analyses revealed aragonite as the main mineral, with minor quartz content limited only to the oldest portion of the studied period. Furthermore, large variation of the centered log ratio transformed variables of Sr and Ca with detrital elements such as Ti and Al (Supporting file) and small variations between Sr and Ca with inorganic carbon (INC) (Supporting file) additionally confirm that Sr and Ca vastly represent carbonate component and are not of detrital origin.

Finally, the Sr budget of the Lake Veliko jezero water and consequently the Sr/Ca ratio of the bulk sediment can also be influenced by hydrological variability. Changes in hydrological regime would theoretically affect relative marine influence at this location because of a limited connection of the lake to the Adriatic Sea through permeable karst: the ocean water is characterized by higher Sr concentration compared to the freshwater (Martin & Meybeck, 1979). Two possible scenarios emerge if hydrologically induced Sr availability was the limiting factor for Sr/Ca ratio of the bulk sediment.

Firstly, during cold periods, Sr/Ca in the lake water would be lower because of reduced evaporation rate i.e. decreased marine influence. This would finally result in a relative decrease in Sr concentration of the lake water and consequently Sr/Ca of the lake sediments. The opposite would be the case for warmer climate conditions. This scenario however can be discarded based upon good correlation of maxima in our Sr/Ca record with cold events which were previously observed in multiple paleoclimate archives in the Mediterranean region (Figure 3). In the figure 3 locally estimated scatterplot smoothed (LOESS) Sr/Ca curve, with smoothing factor of 0.09, displays four distinct peaks centred at 8.3, 6.0, 4.25 and 2.9 cal ka BP. First Sr/Ca maxima in our record, centred at 8.3 ka is coeval to cold event described in pollen record from the Adriatic Sea by Combourieu-Nebout et al., (2013) and drop in the sea surface temperature (Siani et al., 2013) recognized in the same core. In Alboran Sea drop in the temperature at that time period was recorded as well (Cacho et al., 2001; Fletcher et al, 2012) while minor drop in the temperature was also observed in the Gemini lake (Samartin et al., 2017). These events correlate with the North Atlantic cold event (NAC5) described by Bond et al. (2001). Following the pluvial period (7.6 to 7 cal ka BP) characterised by Mg-Calcite deposition instead of aragonite, another maxima in Sr/Ca record from M1-A core, centred at about 6 cal ka BP, can be correlated with cold spells recognized in the Adriatic (Sangiorgi et al., 2003; Combourieu-Nebout et al., 2013), Tyrrhenian and less clearly in Alboran sea (Cacho et al., 2001) as well as NAC4 event in the North Atlantic (Bond et al., 2001). Temperature reconstructions based on chironomid communities from Gemini and Verdarolo lakes also indicate cold conditions at around 6 cal ka BP (Samartin et al., 2017). A Sr/Ca maxima at about 4.25 cal ka BP is correlated to a decrease in the temperature in the Adriatic Sea and Italian lakes (Combourieu-Nebout et al., 2013; Samartin et al., 2017) and in the North (Bond et al., 2001). Finally, an increase in the Sr/Ca centred at about 2.9 cal ka BP correlates well with the cold spells already recognized in the Adriatic, Alboran and Tyrrhenian Sea (Cacho et al., 2001; Sangiorgi et al., 2003; Fletcher et al., 2012; Combourieu-Nebout et al., 2013) as well as in the North Atlantic (Bond et al., 2001). A less pronounced temperature decrease during this time interval was observed in Lake Gemini, Italy (Samartin et al., 2017).

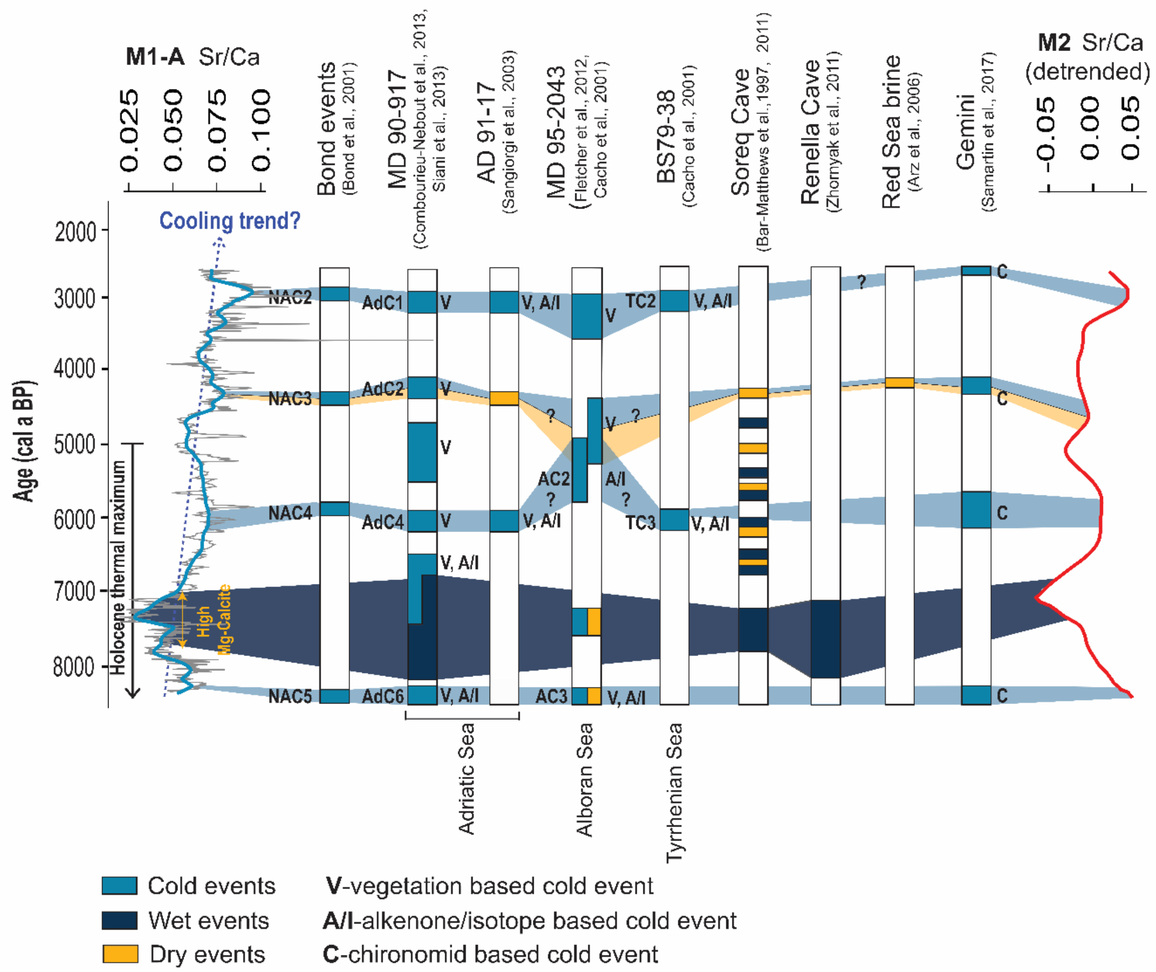

Figure 3. Sr/Ca records for Cores M1 and M2 as indicator of relative palaeotemperature and palaeohydrology compared to palaeotemperature and palaeohydrological proxies from other records from the wider Mediterranean region. The Mg-calcite rich interval is underlain by a dark blue area in the Sr/Ca record. Otherwise needle-like aragonite is the dominant phase. NAC, AdC, AC, TC are abbreviations for cold events based on original publications.

Second scenario implies that the environment during cold events was also dry, while during warmer events it was more wet. This would lead to a decreased relative marine influence and the dilution of the Sr budget in the lake water, which would finally result in lower Sr/Ca during warm periods and higher values during the cold periods. To further investigate the role of wet versus dry conditions potentially driving the Sr/Ca variability we studied additional chemical elements acquired by XRF scanning like Br, Rb, Si, K, Na, Al, Fe, Mn, Zr, Ti and Mo, most of them validated by wet-chemical analysis on discrete samples, e.g. through ICP-MS. We used all of these elements to model proxies called balances for palaeotemperature, aeolian input and palaeoredox conditions. This was done through orthonormal log ratio transformation (Egozcue & Pawlowsky-Glahn, 2019) which enabled firm statistical parameter to be established for reliable interpretation of involved processes (Razum et al., 2020b). The methodology is fully explained in Razum et al., 2020b and is given briefly in supporting material. In the end five balances were modelled, each is a proxy for certain process; b3 and b4 are proxies for palaeoredox conditions, b5 is a proxy for aeolian activity while b2 is a

palaeoclimate proxy equivalent to Sr/Ca (rationale for balance construction is shown in supporting file).
The data analyses show that an increase in Sr/Ca correlates to increases in anoxic conditions ($r_{(b2-b3)}$ = 0.55, $p_{(0.05)}$ = 0.00001) and aeolian activity ($r_{(b2-b5)}$ = 0.56, $p_{(0.05)}$ = 0.00001) (Figure 4). Furthermore, a speleothem based palaeohydrological reconstruction from Corchia cave in Italy (Regattieri et al., 2014) implies that during the time of Sr/Ca maxima in our record climate conditions were generally drier (Figure 4). However, it is also evident that Sr/Ca ratios in our record do not exhibit exceptionally high values during the most widespread dry event in the Mediterranean and wider region at 4.2 ka (Sangiorgi et al., 2003; Arz et al., 2006; Drysdale et al., 2006; Magny et al., 2009; Bar-Matthews & Ayalon, 2011; Bini et al., 2019). This implies that hydrological conditions probably played, compared to the temperature effect, less of a role in driving Sr/Ca ratios. Following all lines of evidences, we propose that the Sr/Ca ratio of Lake Veliko jezero bulk sediment is representing Sr/Ca ratio of inorganic needle-like aragonite

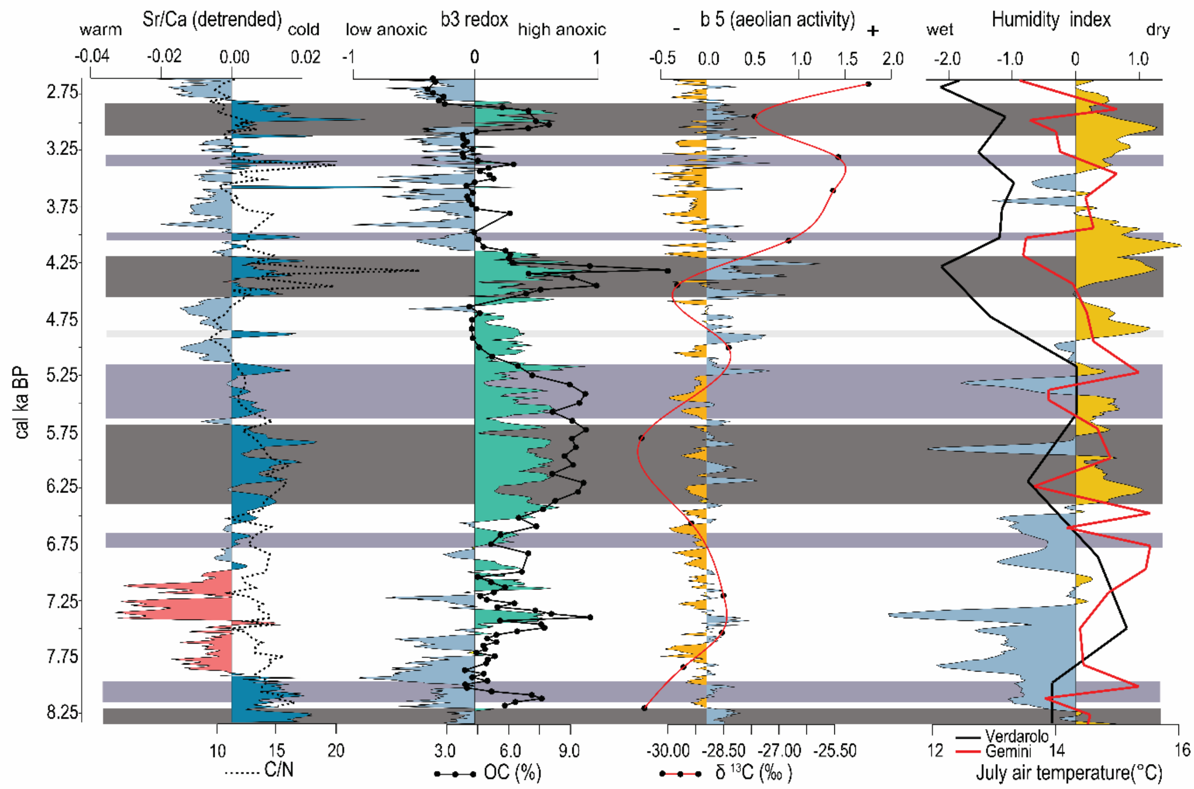

Figure 4. Sr/Ca (3-point average curves), 'Balances b3?' (redox) and 'b5' (aeolian input) derived from the XRF data and its connection with organic matter data (C/N, OC and $\delta^{13}C$). Gray bands inidcate main cold events, purple bands are minor cold events recognized in M1-A. Correlation of those events with temperature changes in Lakes Gemini and Verdarolo and humidity index from Corchia are visible on the right side of the figure.

that mainly reflects relative palaeotemperature changes while hydrological variability likely playing a secondary role.

One of the main advantages of XRF core scanning despite being non-destructive is the high resolution. If Sr/Ca ratios is a temperature indicator, then it is maybe also applicable for short events, for example we observe several, relatively brief cold events at 8.0, 6.6, 5.4, 4.8, 4.0 and 3.3 cal ka BP. From these, the events at 8.0, 6.6, 5.4 and 4.0 cal ka BP were also recorded in Lake Gemini, while the 3.3 ka BP event was recognized in Lake Verdarolo (Samartin et al., 2017). Most of these events are characterized by an increase in anoxic conditions and aeolian input, indicating not only cooler but also drier climate conditions at our sites (Figure 4). These events can be detected due to the combined effects of the limited size and detrital influence on the studied lake(s) and high-resolution data. The small size of this lake (surface area of 1.44 km^2) with very limited detrital influence i.e. small effects of internal and landscape filters as defined in Blenckner (2005) results into increased sensitivity in recording smaller-scale climate events.

2.3. Disentangling the drivers of OC burial efficiency

To decipher potential drivers of OC burial efficiency we analyzed OC, inorganic carbon (INC) and organic nitrogene (N) and explored its relationship with enhanced anoxic episodes, cold spells and aeolian input. Additionally, to better characterize the provenance of organic matter (OM) we analyzed $\delta^{13}C$ throughout the same interval.

Higher C/N ratios (>10) indicate potential mixing of the land-derived and autochthonous organic matter (Meyers & Ishiwatari, 1993; Meyers, 1994), while more negative $\delta^{13}C$ values could also be related to the increase of the land-derived component of the organic matter (Lamb et al., 2006). Our results demonstrate a slight long-term decreasing trend in C/N record coinciding with a much stronger increasing trend of $\delta^{13}C$ values. This anticorrelated pattern of the two proxies indicates that land-derived organic matter is partly decreasing in line with the overall detrital influence during our studied interval (Figure 4). Additional evidence comes from the occurrence of quartz only found at the base of the studied interval (supporting file). A combination of two factors is most probably causing the described trends. First, lake deepening caused by the Holocene sea level rise, moved shoreline away from the core site. More specifically, the distance between Core M1-A and the Pomena doline which is a small terra rossa soil patch adjacent to Lake Veliko jezero (Pomena field, Figure 1) was increased. Second, due to the Holocene sea level rise a gradual increase in marine influence through the permeable karst did occur. The sea level rise changed the lake biota (Wunsam et al., 1999) and consequently organic carbon content and composition.

During the studied interval just two different pollen zones occurred, one with *Juniperus* and *Phillyrea* at ca. 8 to 6.5 ka BP and another of *Quercus ilex* from 6.5 ka BP to present (Jahns & Bogaard, 1998). This finding implies minor changes in the terrestrial vegetation with negligible impact on carbon content, composition and variability.

The correlation of the OC content with Sr/Ca record reflecting temperature variations on millennial time scale suggests that the OC content increased during cold interludes (Figure 4). The observed OC increase during cold events is in line with a study of Gudasz et al. (2010) where a temperature decrease leads to low mineralization of OC. However, the temperature effect through OC mineralization was not the substantial factor for OC preservation in the Lake Veliko jezero sediments. If temperature was driving the OC preservation on millennial time scales, cold climate conditions would decrease the degradation rate of algal (autochthonous) organic matter (Sampei & Matsumoto, 2001). This would result in all lower C/N values, higher OC and more positive $\delta^{13}C$ values, which we did not see in our data. Indeed, we observe slightly higher C/N and more negative $\delta^{13}C$ values during cold spells. This would imply that land-sourced organic matter increased during cold spells as a result of enhanced aeolian input, confirmed by correlation analyses *r(b2-b5)* (Figure 4). Yet, we argue that an increase in land-sourced organic matter is not the main mechanism in overall OC increase. If this would have been the case, then one would expect that more than double increase in OC during the cold spells would cause substantial increase in C/N, which is not observed in our record. An exception is the 4.2 event, when maximum C/N ratios occurred.

The OC amount and variability also correlates with paleoredox proxy (Figure 4), i.e. an increase in anoxic conditions corresponds to an increase in OC content. Based on this finding we propose that an increase in anoxic conditions is the main factor that led to OC preservation at our site. Decrease in temperature and possibly drier conditions during cold events would shift the redox zone boundary and thermocline closer to the surface (Zadereev et al., 2014). This would prevent mixing of the water throughout the water body, thus causing the anoxic boundary to move upward, leaving the majority of the water column under anoxic conditions. This is also confirmed by high correlation between palaeotemperature (b2) and palaeoredox (b3) proxies. Although the depth of a thermocline depends on a number of factors such as lake size, dissolved organic content, temperature, wind activity etc. (summarized in Cantin et al., (2011) we believe that the temperature was the key factor controlling thermocline and redox zone boundary depth in Lake Veliko jezero. These findings are underpinned by a study of modern processes in Lake Veliko jezero lake, where the thermocline occurs only during summer months (Benović et al., 2000). Finally, a shallow thermocline/redox zone boundary would cause that most of the organic matter produced in and transported into the lake is prevented from decomposing resulting in higher OC values during cold spells.

3. Conclusions

Data presented demonstrate that temperature changes may have a significant impact on OC burial efficiency. Temperature decrease and likely drier climate conditions caused shifting of anoxic boundary towards the surface of the lake and thus prevented OC mineralization in an oxic environment. This study is, unlike many previous studies, unbiased in respect to the anthropogenic influence, changes in latitude or significant vegetation changes, which might have an effect on OC burial efficiency. Our results demonstrate that climate variability was able to trigger mechanisms inherent to the lake resulting into oscillations of OC burial efficiency.

The Sr/Ca ratio of bulk sediment reflects the formation of aragonite needles in this special lake setting, and is a novel approach that can be utilized for paleoclimate reconstructions. We were able to identify several cooling events known in the wider Mediterranean area, but the unique high resolution of our data enabled to also identify a number of short-term cold and dry events throughout the 8.3 to 2.6 cal ka BP period that mainly have not been found before. Further high-resolution studies on additional archives would be beneficial for investigating their wider regional character.

Acknowledgments

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References:

Aitchison, J., & Greenacre, M. (2002). Biplots of compositional data. *Journal of the Royal Statistical Society. Series C: Applied Statistics*, 51(4), 375–392. https://doi.org/10.1111/1467-9876.00275

Algesten, G., Sobek, S., Bergstrom, A.-K., Ågren, A., Tranvik, L. J., & Jansson, M. (2003). Role of lakes for organic carbon cycling in the boreal zone. *Global Change Biology*, 10, 141–147. https://doi.org/10.1046/j.1529-8817.2003.00721.x

Anderson, N. J., Dietz, R. D., & Engstrom, D. R. (2013). Land-use change, not climate, controls organic carbon burial in lakes. *Proceedings of the Royal Society B: Biological Sciences*, 280(1769). https://doi.org/10.1098/rspb.2013.1278

Anderson, N. J., Heathcote, A. J., Engstrom, D. R., Ryves, D. B., Mills, K., Prairie, Y. T., et al. (2020). Anthropogenic alteration of nutrient supply increases the global freshwater carbon sink. *Science Advances*, 6(16), 1–9. https://doi.org/10.1126/sciadv.aaw2145

Arz, H. W., Lamy, F., & Pätzold, J. (2006). A pronounced dry event recorded around 4.2 ka in brine sediments from the northern Red Sea. *Quaternary Research*, 66(3), 432–441. https://doi.org/10.1016/j.yqres.2006.05.006

Bar-Matthews, M., Ayalon, A., & Kaufman, A. (1998). Middle to Late Holocene (6,500 Yr. Period) Paleoclimate in the Eastern Mediterranean Region from Stable Isotopic Composition of Speleothems from Soreq Cave, Israel. In Issar, A. S., Brown, N. (Eds.), *Water, Environment and Society in times of climate change*, 203–214. https://doi.org/10.1007/978-94-017-3659-6_9

Bar-Matthews, M., & Ayalon, A. (2011). Mid-Holocene climate variations revealed by high-resolution speleothem records from Soreq cave, Israel and their correlation with cultural changes. *Holocene*, 21(1), 163–171. https://doi.org/10.1177/0959683610384165

Bar-Matthews, M., Ayalon, A., & Kaufman, A. (1997). Late Quaternary Paleoclimate in the Eastern Mediterranean Region from Stable Isotope Analysis of Speleothems at Soreq Cave, Israel. *Quaternary Research*, 47(2), 155–168. https://doi.org/10.1006/qres.1997.1883

Bartosiewicz, M., Przytulska, A., Lapierre, J., Laurion, I., Lehmann, M. F., & Maranger, R. (2019). Hot tops, cold bottoms: Synergistic climate warming and shielding effects increase carbon burial in lakes. *Limnology and Oceanography Letters*, 4(5), 132–144. https://doi.org/10.1002/lol2.10117

Beck, J. W., Edwards, R. L., Ito, E., Taylor, F. W., Recy, J., Rougerie, F., et al. (1992). Sea-Surface Temperature from Coral Skeletal Strontium/Calcium Ratios. *Science*, 257, 0–3.

Benović, A., Lučić, D., Onfori, V., Peharda, M., Carić, M., Jasprica, N., & Bobanović-Ćolić, S. (2000). Ecological characteristics of the Mljet Island seawater lakes (South Adriatic Sea) with special reference to their resident populations of medusae. *Scientia Marina*, 64(S1), 197–206. https://doi.org/10.3989/scimar.2000.64s1197

Blenckner, T. (2005). A conceptual model of climate-related effects on lake ecosystems. *Hydrobiologia*, 533(1), 1–14. https://doi.org/10.1007/s10750-004-1463-4

Bond, G., Kromer, B., Beer, J., Muscheler, R., Evans, M. N., Showers, W., et al. (2001). Persistent solar influence on North Atlantic climate during the Holocene. *Science*, 294(5549), 2130–2136. https://doi.org/10.1126/science.1065680

Cacho I., Grimal J., Canals M., Sbaffi L., Shackleton N., Schönfeld J., & Zahn. R. (2001). Variability of the western Mediterranean Sea surface temperature during the last 25000 years and its connection with the Northern Hemisphere climate changes. *Paleoceanography and Paleoclimatology*, 16(1), 40–52. https://doi.org/10.1029/2000PA000502

Cantin, A., Beisner, B. E., Gunn, J. M., Prairie, Y. T., & Winter, J. G. (2011). Effects of thermocline deepening on lake plankton communities. *Canadian Journal of Fisheries and Aquatic Sciences*, 68(2), 260–276. https://doi.org/10.1139/F10-138

Carey, C. C., Doubek, J. P., McClure, R. P., & Hanson, P. C. (2018). Oxygen dynamics control the burial of organic carbon in a eutrophic reservoir. *Limnology and Oceanography Letters*, 3(3), 293–301. https://doi.org/10.1002/lol2.10057

Comas, M., & Thió-Henestrosa, S. (2011). CoDaPack 2.0: a stand-alone, multi-platform compositional software. In J. J. Egozcue, R. Tolosana-Delgado, & M. I. Ortego (Eds.), *Proceedings of the 4th International Workshop on Compositional Data Analysis (2011)*.

Combourieu-Nebout, N., Peyron, O., Bout-Roumazeilles, V., Goring, S., Dormoy, I., Joannin, S., et al. (2013). Holocene vegetation and climate changes in the central Mediterranean inferred from a high-resolution marine pollen record (Adriatic Sea). *Climate of the Past*, 9(5), 2023–2042. https://doi.org/10.5194/cp-9-2023-2013

Corrège, T. (2006). Sea surface temperature and salinity reconstruction from coral geochemical tracers. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 232(2–4), 408–428. https://doi.org/10.1016/j.palaeo.2005.10.014

Dietzel, M., Gussone, N., & Eisenhauer, A. (2004). Co-precipitation of Sr^{2+} and Ba^{2+} with aragonite by membrane diffusion of CO_2 between 10 and 50 °C. *Chemical Geology*, 203(1–2), 139–151. https://doi.org/10.1016/j.chemgeo.2003.09.008

Drysdale, R., Zanchetta, G., Hellstrom, J., Maas, R., Fallick, A., Pickett, M., et al. (2006). Late Holocene drought responsible for the collapse of Old World civilizations is recorded in an Italian cave flowstone. *Geology*, 34(2), 101–104. https://doi.org/10.1130/G22103.1

Egozcue, J. J., & Pawlowsky-Glahn, V. (2019). Compositional data: the sample space and its structure. *Test*, 28(3), 599-638. https://doi.org/10.1007/s11749-019-00670-6

Fletcher, W. J., Debret, M., & Sanchez Goñi, M. (2012). The Holocene frequency millennial oscillation in western Mediterranean climate: Implications for past dynamics of the North Atlantic atmospheric westerlies. *The Holocene*, 23(2), 153–166. https://doi.org/10.1177/0959683612460783

Gudasz, C., Bastviken, D., Steger, K., Premke, K., Sobek, S., & Tranvik, L. J. (2010). Temperature-controlled organic carbon mineralization in lake sediments. *Nature*, 466(7305), 478–481. https://doi.org/10.1038/nature09186

Gudasz, C., Sobek, S., Bastviken, D., Koehler, B., & Tranvik, L. J. (2015). Temperature sensitivity of organic carbon mineralization in contrasting lake sediments. *Journal of Geophysical Research: Biogeosciences*, 120(7), 1215–1225. https://doi.org/10.1002/2015JG002928

Heathcote, A. J., Anderson, N. J., Prairie, Y. T., Engstrom, D. R., & Del Giorgio, P. A. (2015). Large increases in carbon burial in northern lakes during the Anthropocene. *Nature Communications*, 6, 1–6. https://doi.org/10.1038/ncomms10016

Helz, G. R., Miller, C. V., Charnock, J. M., Mosselmans, J. F. W., Pattrick, R. A. D., Garner, C. D., & Vaughan, D. J. (1996). Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence. *Geochimica et Cosmochimica Acta*, 60(19), 3631–3642. https://doi.org/10.1016/0016-7037(96)00195-0

Jahns, S., & Bogaard, C. (1998). New palynological and tephrostratigraphical investigations of two salt lagoons on the island of Mljet, south Dalmatia, Croatia. *Vegetation History and Archaeobotany*, 7(4), 219–234. https://doi.org/10.1007/BF01146195

Kallel, N., Paterne, M., Duplessy, J. C., Vergnaud-Grazzini, C., Pujol, C., Labeyrie, L., et al. (1997). Enhanced rainfall in the Mediterranean region during the last Sapropel Event. *Oceanologica Acta*, 20(5), 697–712. https://doi.org/http://dx.doi.org/10.1016/S0031-0182(97)00021-7

Kinsman, J. J., & Holland, H. D. (1969). The co-precipitation of cations with $CaCO_3$ - IV. The co-precipitation of Sr^{2+} with aragonite between 16° and 96°C. *Geochimica et Cosmochimica Acta*, 33(October 1964), 1–17. https://doi.org/10.1016/0016-7037(69)90089-1

Kitano, Y., Kanamori, N., & Oomori, T. (1971). Measurements of distribution coefficients of strontium and barium between carbonate precipitate and solution —Abnormally high values of distribution coefficients measured at early stages of carbonate formation. *Geochemical Journal*, 4(4), 183–206. https://doi.org/10.2343/geochemj.4.183

Lamb, A. L., Wilson, G. P., & Leng, M. J. (2006). A review of coastal paleoclimate and relative sea-level reconstructions using $\delta^{13}C$ and C/N ratios in organic material. *Earth-Science Reviews*, 75(1–4), 29–57. https://doi.org/10.1016/j.earscirev.2005.10.003

Larsen, S., Andersen, T., & Hessen, D. O. (2011). Climate change predicted to cause severe increase of organic carbon in lakes. *Global Change Biology*, 17(2), 1186–1192. https://doi.org/10.1111/j.1365-2486.2010.02257.x

McManus, J., Berelson, W. M., Severmann, S., Poulson, R. L., Hammond, D. E., Klinkhammer, G. P., & Holm, C. (2006). Molybdenum and uranium geochemistry in continental margin sediments: Paleoproxy potential. *Geochimica et Cosmochimica Acta, 70*(18), 4643–4662. https://doi.org/10.1016/j.gca.2006.06.1564

Magny, M., Peyron, O., Sadori, L., Ortu, E., Zanchetta, G., Vannière, B., & Tinner, W. (2012). Contrasting patterns of precipitation seasonality during the Holocene in the south- and north-central Mediterranean. *Journal of Quaternary Science*, 27(3), 290–296. https://doi.org/10.1002/jqs.1543

Magny, M., Vannière, B., Zanchetta, G., Fouache, E., Touchais, G., Petrika, L., et al. (2009). Possible complexity of the climatic event around 4300-3800 cal. BP in the central and western Mediterranean. *Holocene*, 19(6), 823–833. https://doi.org/10.1177/0959683609337360

Martin, J., & Meybeck, M. (1979). Elemental mass-balance of material carried by major world rivers. *Marine Chemistry*, 7, 173–206. https://doi.org/10.1016/0304-4203(79)90039-2

Mendonça, R., Müller, R. A., Clow, D., Verpoorter, C., Raymond, P., Tranvik, L. J., & Sobek, S. (2017). Organic carbon burial in global lakes and reservoirs. *Nature Communications*, 8(1), 1–6. https://doi.org/10.1038/s41467-017-01789-6

Meyers, P. A. (1994). Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology*, 114, 289–302. https://doi.org/10.1016/0009-2541(94)90059-0

Meyers, P. A., & Ishiwatari, R. (1993). Lacustrine organic geochemistry-an overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic Geochemistry*, 20(7), 867–900. https://doi.org/10.1016/0146-6380(93)90100-P

Pawlowsky-Glahn, V., Egozcue, J. J., & Tolosana-Delgado, R. (2015). *Modelling and analysis of compositional data*. Chichester (UK), John Wiley & Sons, https://doi.org/10.1017/CBO9781107415324.004

Razum, I., Miko, S., Ilijanić, N., Petrelli, M., Röhl, U., Hasan, O., & Giaccio, B. (2020a). Holocene tephra record of Lake Veliko jezero, Croatia: implications for the central Mediterranean tephrostratigraphy and sea level rise. *Boreas*, 49(3), 653-673. https://doi.org/10.1111/bor.12446

Razum, I., Miko, S., Ilijanić, N., Hasan, O., Šparica Miko, M., Brunović, D., Pawlowsky-Glahn, V. (2020b). A compositional approach to the reconstruction of geochemical processes involved in the evolution of Holocene marine flooded coastal karst basins (Mljet Island, Croatia). *Applied Geochemistry*, 116, 104574. https://doi.org/10.1016/j.apgeochem.2020.104574

Regattieri, E., Zanchetta, G., Drysdale, R. N., Isola, I., Hellstrom, J. C., & Dallai, L. (2014). Late Glacial to Holocene trace element record (Ba, Mg, Sr) from Corchia Cave (Apuan Alps, central Italy): Paleoenvironmental implications. *Journal of Quaternary Science*, 29(4), 381–392. https://doi.org/10.1002/jqs.2712

Samartin, S., Heiri, O., Joos, F., Renssen, H., Franke, J., Brönnimann, S., & Tinner, W. (2017). Warm Mediterranean mid-Holocene summers inferred from fossil midge assemblages. *Nature Geoscience*, 10(3), 207–212. https://doi.org/10.1038/ngeo2891

Sampei, Y., & Matsumoto, E. (2001). C/N ratios in a sediment core from Nakaumi Lagoon, southwest Japan -usefulness as an organic source indicator-. *Geochemical Journal*, 35, 189–205. https://doi.org/10.2343/geochemj.35.189

Sangiorgi, F., Capotondi, L., Combourieu Nebout, N., Vigliotti, L., Brinkhuis, H., Giunta, S., et al. (2003). Holocene seasonal sea-surface temperature variations in the southern Adriatic Sea inferred from a multiproxy approach. *Journal of Quaternary Science*, 18(8), 723–732. https://doi.org/10.1002/jqs.782

Scott, C., & Lyons, T. W. (2012). Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: Refining the paleoproxies. *Chemical Geology*, 324–325, 19–27. https://doi.org/10.1016/j.chemgeo.2012.05.012

Shimmield, G. B., & Price, N. B. (1986). The behaviour of molybdenum and manganese during early sediment diagenesis - offshore Baja California, Mexico. *Marine Chemistry*, 19(3), 261–280. https://doi.org/10.1016/0304-4203(86)90027-7

Siani, G., Magny, M., Paterne, M., Debret, M., & Fontugne, M. (2013). Paleohydrology reconstruction and Holocene climate variability in the South Adriatic Sea. *Climate of the Past*, 9(1), 499–515. https://doi.org/10.5194/cp-9-499-2013

Sobek, S., Anderson, N. J., Bernasconi, S. M., & Del Sontro, T. (2014). Low organic carbon burial efficiency in arctic lake sediments. *Journal of Geophysical Research: Biogeosciences*, 119(6), 1231–1243. https://doi.org/10.1002/2014JG002612

Sobek, S., Algesten, G., Bergström, A. K., Jansson, M., & Tranvik, L. J. (2003). The catchment and climate regulation of pCO_2 in boreal lakes. *Global Change Biology*, 9(4), 630–641. https://doi.org/10.1046/j.1365-2486.2003.00619.x

Sobek, S., Durisch-Kaiser, E., Zurbrugg, R., Wongfun, N., Wessels, M., Pasche, N., & Wehrli, B. (2009). Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. *Limnology and Oceanography*, 54(6), 2243–2254. https://doi.org/10.4319/lo.2009.54.6.2243

Sondi, I., & Juračić, M. (2010). Whiting events and the formation of aragonite in Mediterranean karstic marine lakes: New evidence on its biologically induced inorganic origin. *Sedimentology*, 57(1), 85–95. https://doi.org/10.1111/j.1365-3091.2009.01090.x

Templ, M., Hron, K., & Filzmoser, P. (2011). robCompositions: a R-package for robust statistical analysis of compositional data. In V. Pawlowsky-Glahn and A. Buccianti (Eds.), *Compositional Data Analysis. Theory and Applications*, pp. 341-355, London, John Wiley & Sons

Tribovillard, N., Algeo, T. J., Lyons, T., & Riboulleau, A. (2006). Trace metals as paleoredox and paleoproductivity proxies: An update. *Chemical Geology*, 232(1–2), 12–32. https://doi.org/10.1016/j.chemgeo.2006.02.012

Vorlicek, T. P., Kahn, M. D., Kasuya, Y., & Helz, G. R. (2004). Capture of molybdenum in pyrite-forming sediments: Role of ligand-induced reduction by polysulfides. *Geochimica et Cosmochimica Acta*, 68(3), 547–556. https://doi.org/10.1016/S0016-7037(00)00444-7

Wunsam, S., Schmidt, R., & Müller, J. (1999). Holocene lake development of two dalmatian lagoons (Malo and Veliko Jezero, Isle of Mljet) in respect to changes in Adriatic Sea level and climate. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 146(1–4), 251–281. https://doi.org/10.1016/S0031-0182(98)00147-3

Xu, H., Lan, J., Liu, B., Sheng, E., & Yeager, K. M. (2013). Modern carbon burial in Lake Qinghai, China. *Applied Geochemistry*, 39(April), 150–155. https://doi.org/10.1016/j.apgeochem.2013.04.004

Zadereev, E. S., Tolomeev, A. P., Drobotov, A. V., & Kolmakova, A. A. (2014). Impact of weather variability on spatial and seasonal dynamics of dissolved and suspended nutrients in water column of meromictic Lake Shira. *Contemporary Problems of Ecology*, *7*(4), 384–396. https://doi.org/10.1134/S199542551404012X

Zheng, Y., Anderson, R. F., Van Geen, A., & Kuwabara, J. (2000). Authigenic molybdenum formation in marine sediments: A link to pore water sulfide in the Santa Barbara Basin. *Geochimica et Cosmochimica Acta*, 64(24), 4165–4178. https://doi.org/10.1016/S0016-7037(00)00495-6

Zhornyak, L. V., Zanchetta, G., Drysdale, R. N., Hellstrom, J. C., Isola, I., Regattieri, E., et al. (2011). Stratigraphic evidence for a “pluvial phase” between ca 8200-7100 ka from Renella cave (Central Italy). *Quaternary Science Reviews*, 30(3–4), 409–417. https://doi.org/10.1016/j.quascirev.2010.12.003