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Natural and human-induced environmental change in southern Albania for the last 300 years — Constraints from the Lake Butrint sedimentary record

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ABSTRACT

A sediment core from Lake Butrint in southwestern Albania contains an annually-layered sequence covering the last ~300 years. It provides thus an exceptionally well-dated time series to study past climate-driven environmental changes, as well as anthropogenic perturbations along the coast of the Ionian Sea. The varves are composed of organic-rich carbonate couplets and detritus-dominated clay layers. The first are deposited during spring-to-fall, and reflect the chemistry of the lake, which, in turn, is sensitive to 1) the relative importance of marine versus freshwater inputs, 2) relative evaporation rates, and 3) the productivity cycle within the lake. The detrital laminae are deposited during winter, reflecting precipitation and runoff conditions during the wet season. A 2–3‰ stable carbon isotope ratio shift in both bulk organics and authigenic carbonates was attributed to increasing eutrophication towards the end of the 20th century, and validated by historical and instrumental data. An increase in the $\delta^{18}\text{O}$ of authigenic carbonates by more than 8‰ indicates the progressive salinization of the lake, which can primarily be attributed to man-made perturbations that reduced the freshwater input to the lake and/or enhanced the exchange with seawater from the nearby Ionian Sea. A recent increase in the relative evaporation versus precipitation rates may have additionally contributed to the observed ^{18}O enrichment in the Lake Butrint carbonates. The interdecadal cyclicity in the thickness of the detrital laminae seems to be at least partially controlled by NAO and/or ENSO-like phenomena that modulate precipitation patterns in the eastern Mediterranean. Thus, this study demonstrates the potential of combining microstratigraphic and stable isotopic tools to disentangle anthropogenic and natural environmental changes in Lake Butrint, validated by historical records.

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1. Introduction

The identification and separation of climatic and human impacts on the environment represent one of the main challenges in present paleoenvironmental research. As an example, coastal areas in the Mediterranean realm have been clearly modified by anthropogenic activities (e.g., Vita-Finzi, 1969; Chester and James, 1991; Hounslow and Chepstow-Lusty, 2004a and references therein). Often, observed changes in the geomorphology were initially related to regional climate change (Vita-Finzi, 1969), although, more detailed studies combined with improved chronologies, have subsequently shown that human contributions to these changes must have been significant (e.g., Davidson, 1980; Lewin et al., 1991; Billi and Rinaldi, 1997). Whether climate has been the forcing, and perhaps the trigger, behind many of the observed human modifications in the environment

remains also a controversial issue. The deconvolution of natural and anthropogenic influences on the environment is even more complex in regions affected by substantial tectonic activity such as the eastern Mediterranean (Meco and Aliaj, 2000). The Balkan region in particular has been affected by many historically-recorded earthquakes (Papa-zachos et al., 2001), which have induced geomorphologic and sedimentological modifications of the landscape.

Lake sediments provide ideal records of environmental changes, not only within the basins themselves but also of their catchments (e.g., Chondrogianni et al., 1996; Watts et al., 1996; Ariztegui et al., 2001; Anselmetti et al., 2007). Thus, lacustrine sediment archives, in particular when combined with good chronological constraints can be instrumental in separating climate, human and tectonic influences on the environment (e.g., Leroy et al., 2002).

Lake Butrint, located in southwestern Albania near the Greek border (Fig. 1), contains an exceptional archive of past and present natural and human-induced environmental changes occurring along the land–sea interface. On its shore, the antique city of Butrint, an UNESCO world heritage site, is a unique archaeological example

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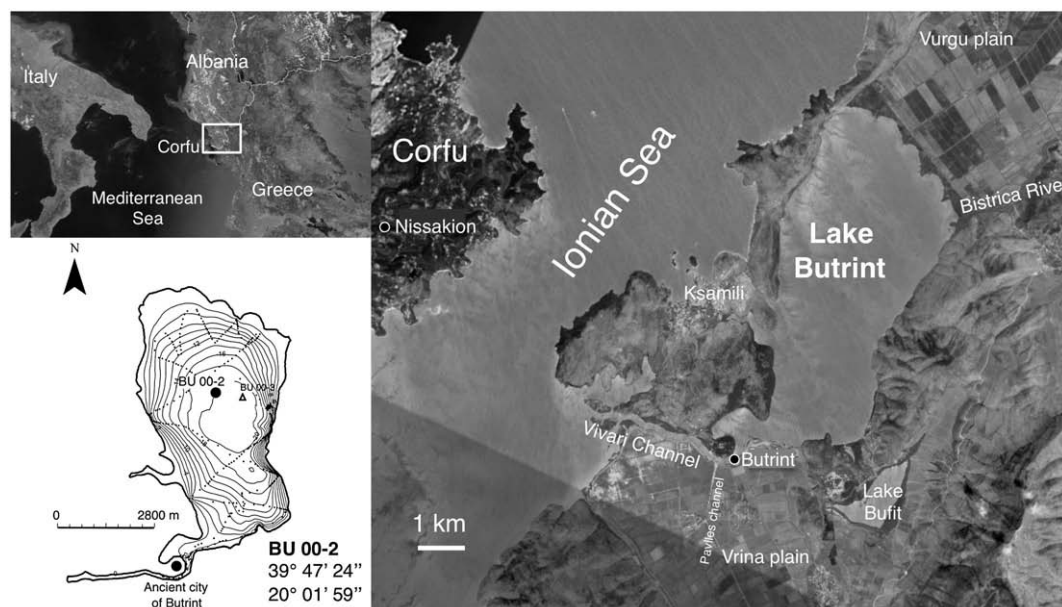


Fig. 1. Satellite image of the Mediterranean area showing the location of Lake Butrint in southern Albania. The close-up view of the study region shows in detail the lake and how the Vivari Channel connects it to the Ionian Sea. Notice the intensive agriculture at both Vurgu and Vrina plains located north and south of the lake, respectively. The bathymetric map shows the location of the two sedimentary cores.

representing a microcosm of Mediterranean history from the archaic Greek until the Venetian cultures, providing an unusual source of continuous documentary data (Hounslow and Chepstow-Lusty, 2004a,b). Although previous archaeological studies have acknowledged environmental (and cultural) change in the Lake Butrint area, the detailed timing and nature of geomorphologic and vegetational changes, for example, are not yet well understood.

Here we present a multi-proxy study of Lake Butrint sediments spanning the last ~300 years. We provide a first comprehensive description of sedimentation patterns and varve formation in the lake. As we will describe in more detail elsewhere (Anselmetti et al. in prep), the lake Butrint sediments represent a sensitive recorder of documented regional seismic activity, a fact that permits the precise dating of distinct sediment layers and thus the establishment of a robust age model. We demonstrate that the sediment archive of Lake Butrint records changes in Mediterranean climate, as well as the anthropogenic impact on both the trophic state and the hydrology of the lake during the last ~300 years. We anticipate that the results from this study yield valuable information that may provide the basis for paleolimnological extrapolation in future studies of longer sediment cores from Lake Butrint.

2. Regional setting

2.1. Geology and tectonics

The territory of Albania has been strongly affected by tectonic movements related to the Alpine/Mediterranean orogenesis. Lake Butrint's origin is a N–S extending graben structure formed during the Pleistocene, which continued to subside during the Quaternary (Aliaj et al., 2001). Submerged Roman and later levels in the archaeological site of Butrint below the current water table indicate some subsidence of unknown origin and lateral extent in the more recent centuries (Lane, 2004).

Albania is located in one of the most tectonically active areas in Europe generating a large number of earthquakes of variable magnitude. Most of them originate along the Adriatic–Ionian zone coinciding with the European plate–Adriatic microplate boundary (Meco and Aliaj, 2000). Moreover, recurrence rates of seismic events have been documented for the 20th century (Muco, 1994).

2.2. Present geography and climate

Mountains cover almost 80% of the surface of Albania whereas the remaining territory corresponds to relatively small and flat areas. The western littoral region at the Mediterranean coast is humid, hosting several coastal lagoons and lakes often separated by sand bars from the Adriatic Sea in the North and the Ionian Sea in the South (Fig. 1). Lake Butrint is the largest of a series of lagoons along the southernmost part of the coast and is the only Albanian lake connected to the Ionian Sea. According to Negroni (2001) the present lake's morphology is of tectonic origin and was invaded by Mediterranean waters during the Holocene transgression. Archeological data further indicate that during Roman times only the NE and the SW portions of the Vrina plain (Fig. 1) were emerged above sea level (Martin, 2004).

The Albanian climate is typical for the south Mediterranean (Meco and Aliaj, 2000). Mean annual precipitation ranges from 1000 to 1400 mm mostly occurring between November and March. These rainy winters are, however, relatively mild with an average temperature of 11 °C, whereas the summer season is generally dry and hot (Lane, 2004). Southern winds dominate during winter and fall whereas North winds prevail during spring and summer. As for other sectors of the Mediterranean, this general pattern has undergone significant temporal variations, most likely in association with the North Atlantic Oscillation (NAO; Luterbacher et al., 1999).

2.3. Modern hydrology and limnology

Today Lake Butrint is a saline lake with an average salinity of 25 PSU (practical salinity units). The hydrology of the catchment area of Lake Butrint comprises the Lake Bui, the Bistrica River, the Pavles channel, and a series of irrigation channels in the Vurgu and Vrina plains located in the north and south of the lake, respectively (Fig. 2A). According to Negroni (2001), there is an additional input of freshwater to the lake through groundwater from the East as well as from the towns located close to the basin (e.g., Ksamili). The whole area is presently under microtidal influence with a tidal range of 30 cm (Negroni 2001; Hounslow and Chepstow-Lusty, 2004a). Mediterranean saline waters can occasionally reach the lake through the Vivari Channel (Fig. 1) during intervals of particularly high tides. Episodic inflow of marine waters through the peninsula along the

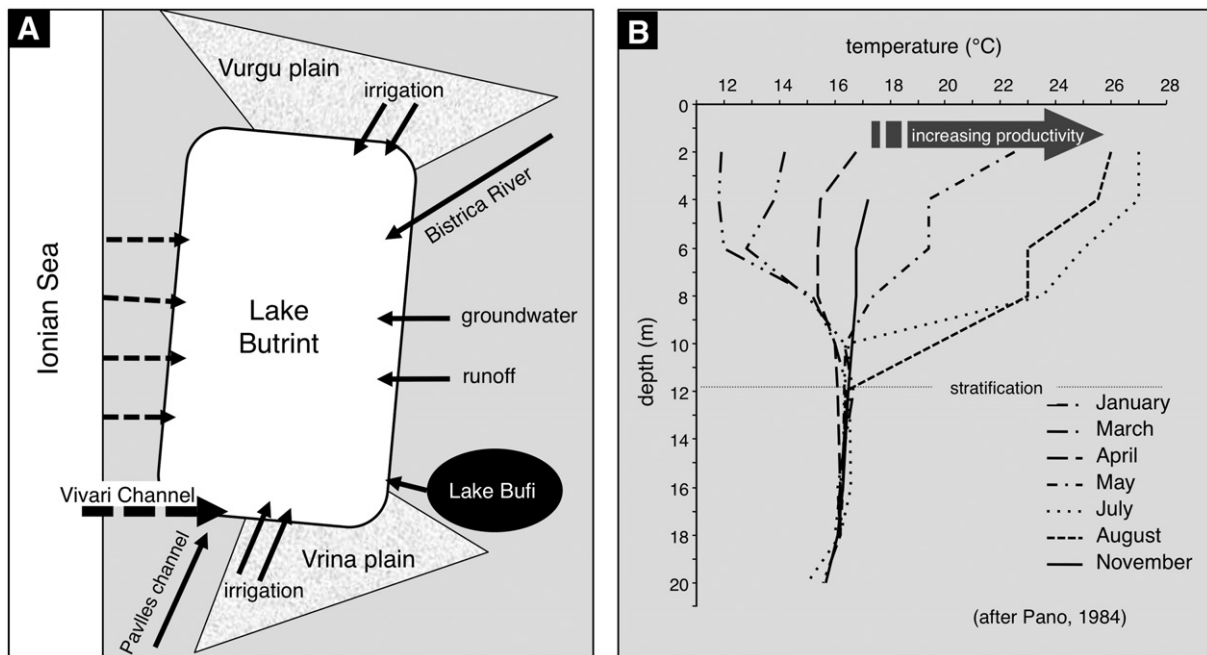


Fig. 2. (A) Simplified hydrological box model for Lake Butrint. Components of the hydrological balance include the exchange with the sea mostly through the Vivari Channel (broken lines), and freshwater input by rivers, irrigations channels in the plains and summer precipitation (solid lines); (B) Water column temperature data (modified from Pano, 1984). Notice the permanent stratification of the water column below ~12 m water depth throughout the year.

western lake shore is also possible. Fig. 2A represents a simple box model indicating the relative input of saline and freshwater sources to the modern lake (after Robbiani, 2005). Their variations (which themselves are anticipated to be sensitive to climate change and/or human impacts) regulate the final salinity of the surface waters that display small seasonal changes (Negroni, 2001).

Modern Lake Butrint has an area of ~1600 ha and a mean water depth of 11.4 m, with a maximum of 21.4 m (Fig. 1). The lake is currently eutrophic, with an estimated total water volume of $\sim 211 \times 10^6 \text{ m}^3$. Water temperature in the surface layer varies seasonally between 12 and 27 °C, but remains constant (~17 °C) throughout the year below ~10 m water depth (Fig. 2B). Due to the strong temperature and salinity gradients, the lake is permanently stratified (Negroni, 2001). This density stratification of the water column generates two well-defined zones that are separated by persistent redox gradients. The uppermost ~8 m of the water column are oxic with salinity varying seasonally and laterally between 13 and 26 PSU whereas below this depth the waters are anoxic/sulfidic with salinities of 30 to 36 PSU (Negroni, 2001). The foot-shaped geometry of the lake together with the freshwater input mostly from the eastern shore result in a rotational movement of surface waters which does not affect the vertical stratification of the lake (Negroni, 2001, Fig. 2B).

2.4. Lake evolution and anthropogenic impact

The hydrological connection of Lake Butrint to the Ionian Sea has changed significantly through history and can explain several limnological features of the present-day basin. During the middle Holocene, the actual lake and the surrounding plains were part of the Mediterranean Sea (Lane, 2004). Indeed, the city of Butrint was initially an important port that became gradually isolated from the sea across the centuries. The aggradation of alluvial material from the Pavlas and Bistrice rivers lead to the generation of prominent deltas and, as a result, the Vivari Channel became the only connection to the Ionian Sea since Roman times. Major hydrological changes also occurred during the 20th century as summarized in Table 1. In 1959 the Bistrice River was diverted to the sea, by-passing Lake Butrint and thus dramatically changing the freshwater budget of the lake. This

man-made modification of the river flow aimed at recovering a large marshy area close to the lake for agricultural purposes. In 1986 and 1987, sediments were dredged out from the Vivari Channel, facilitating the access of saline waters to the lake basin. A re-deviation of the Bistrice River to the lake and the construction of a dam to artificially regulate the water level were accomplished in 1988. The most recent sequence of events has contributed to the dramatic increase in trophic state of the lake since the second half of the 20th century.

3. Material and methods

Bathymetric data were acquired using a Lowrance sonar X-85 (192 kHz) together with a hand-held GPS. The catchment topography was digitalized and geo-referenced from an existing 1:50,000-scale map, and further merged with the bathymetric data using the Surfer® software (Robbiani, 2005). A set of eleven cores was retrieved at different water depths using an ETH-gravity short corer, of which one (BU 00-2, taken in 20 m water depth) is described in detail in this study (see map in Fig. 1). Standard physical properties (density, sonic velocity and magnetic susceptibility) were measured using a GEOTEK® multi-sensor core logger (MSCL) at the Limnogeology Laboratory of the ETH

Table 1

Summary of main anthropogenic changes in the catchment during the 20th century (after Negroni, 2001) and their impact in the lake chemistry and sedimentation.

Years (AD)	Event	Lake response
1930	Starting regular use of fertilizers	Increase eutrophication/anoxia
1946	Expanding agriculture	Increase eutrophication/anoxia
1959	Deviation of Bistrice River	Increase Salinization/eutrophication
1960	Expanding agriculture	Peak eutrophication/anoxia
1986/87	Dredging of the Vivari Channel	Increase Salinization/eutrophication
1987	Expanding agriculture	Peak eutrophication/anoxia
1988	Re-deviation of Bistrice River	Increase Salinization/eutrophication
1996	Increasing agriculture	Increase eutrophication/anoxia

Zürich prior to core opening. These data allowed core correlation throughout the basin.

Individual laminae were first visually counted on both freshly opened cores and high-resolution photographs. Further counting and thickness determination were accomplished using specially tailored image analyses software on high-resolution digital photographs (see Ariztegui et al. 2007 and references therein). An independent chronology for the most recent sediments was obtained by measuring the Cs-137 activity in continuous 0.5 cm thick samples for the uppermost 20 cm. The activity of this radiogenic isotope was determined by γ -spectrometry at the Institute Forel of the University of Geneva.

A first macroscopic description of the sedimentological features of core BU 00-2 was completed in detail using smear slides at selected intervals. SEM observations were carried out with a JEOL JSM6400[®] coupled with an energy-dispersive X-ray detector (EDAX-ISIS) at the Department of Geology and Paleontology, University of Geneva. Mineralogical determinations were accomplished by X-ray diffractometry using a Gandolfi camera (Gandolfi, 1967).

Total organic carbon (TOC) as well as hydrogen and oxygen indices (HI and OI, respectively) were determined by pyrolysis using a Rock-Eval 6[®] at the University of Neuchâtel, Switzerland. Nitrogen content of sediment samples was determined on untreated bulk samples using an elemental analyzer (Carlo-Erba CNS1[®]).

For oxygen (O) and carbon (C) stable isotope ratio determination, authigenic carbonates were reacted at 90 °C with 100% phosphoric acid using an automated carbonate device connected to a VG-Prism mass spectrometer. Fresh sediment samples were first rinsed twice in distilled water and freeze-dried during 48 h prior to measurement in order to eliminate the soluble salt fraction. Prior to C isotope analysis of bulk sedimentary organic matter samples were treated with 1 N HCl to remove carbonate and rinsed with deionized water. After drying, they were loaded into tin sample capsules and measured using a Carlo-Erba CNS2500[®] analyzer with autosampler coupled to a Fisons Optima[®] mass spectrometer. Nitrogen isotopic composition was determined with the same procedure as above but on bulk untreated samples. Carbon isotope values (both organic and inorganic C) are reported in the conventional delta notation with respect to V-PDB. Analytical reproducibility for $\delta^{13}\text{C}$, determined on repeated analyses of NBS-18 and NBS-19 (carbonates), NBS 22 (organic C), as well as internal standards, is better than $\pm 0.1\text{‰}$ for carbonates and better than $\pm 0.2\text{‰}$ for bulk organics. N-isotope ratios are reported with respect to atmospheric nitrogen, and the reproducibility of N-isotope measurements was $\pm 0.2\text{‰}$. All isotopic analyses were carried out at the Geological Institute, ETH Zürich, Switzerland.

4. Results

4.1. Sedimentology

Photographs of two sediment cores (Fig. 3) of Lake Butrint (see bathymetric map in Fig. 1 for core location) document the excellent continuity of the different lithologies in the deepest basin, although the thickness of certain intervals varies. Two end-members lithologies can be discerned: i) exceptionally well laminated sediments with mm-thick laminae; and ii) homogeneous intervals of variable thickness in the mm to cm range (Figs. 3 and 4). The laminated sections comprise 2–3 mm thick dark-brown layers alternating with grayish laminae. At certain depths a third type of laminae that is pure white in color can be observed. Overall, the sediments become darker towards the top of the core whilst the thickness of the gray laminae decreases (Fig. 3). Sedimentological analyses allow the differentiation of several zones in core BU 00-2 as discussed in the following paragraphs. From the bottom of the core to 132.6 cm there are alternating brownish and gray laminae often topped by thinner white laminae decreasing in abundance upwards. A very well developed

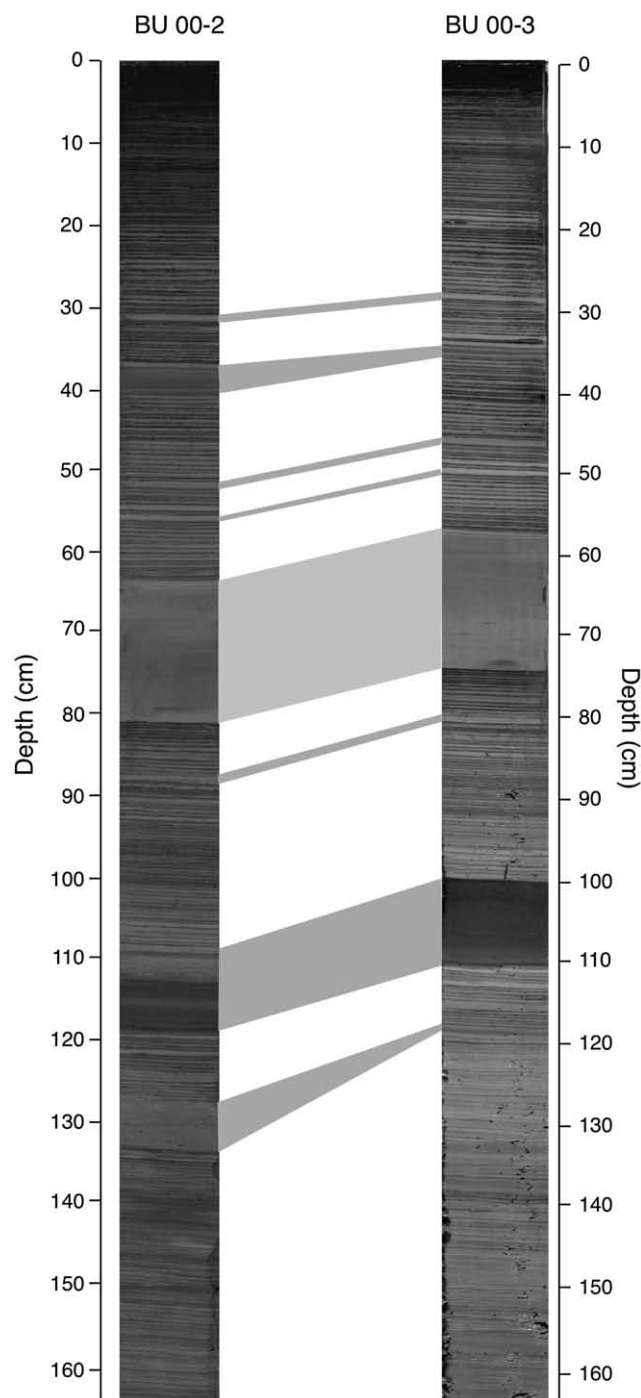


Fig. 3. High-resolution photographs of cores BU 00-2 and BU 00-3 (refer to Fig. 1 for locations). Notice the excellent core-to-core correlation between the two distinctive lithological facies (i.e., laminated and homogeneous sediments).

lamination appears again between 126.2 and 118.2 cm; and 108.2 cm and 101 cm where laminae are very uniform and slightly darker than in the underlying section. The lamination becomes lighter between 101 and 83 cm whereas the uppermost 63 cm contain laminae that progressively darken towards the top of the core, where the lamination fades out.

Smear slides observations indicate that the dark, brownish laminae are composed primarily of amorphous organic matter encompassing centric and mostly pennate diatom frustules as well as carbonate crystals (Fig. 4A). Allochthonous oxidized organic matter (e.g., wood and tree leaf fragments) and, even more importantly, clay particles are the main components of the gray laminae. The thin white laminae

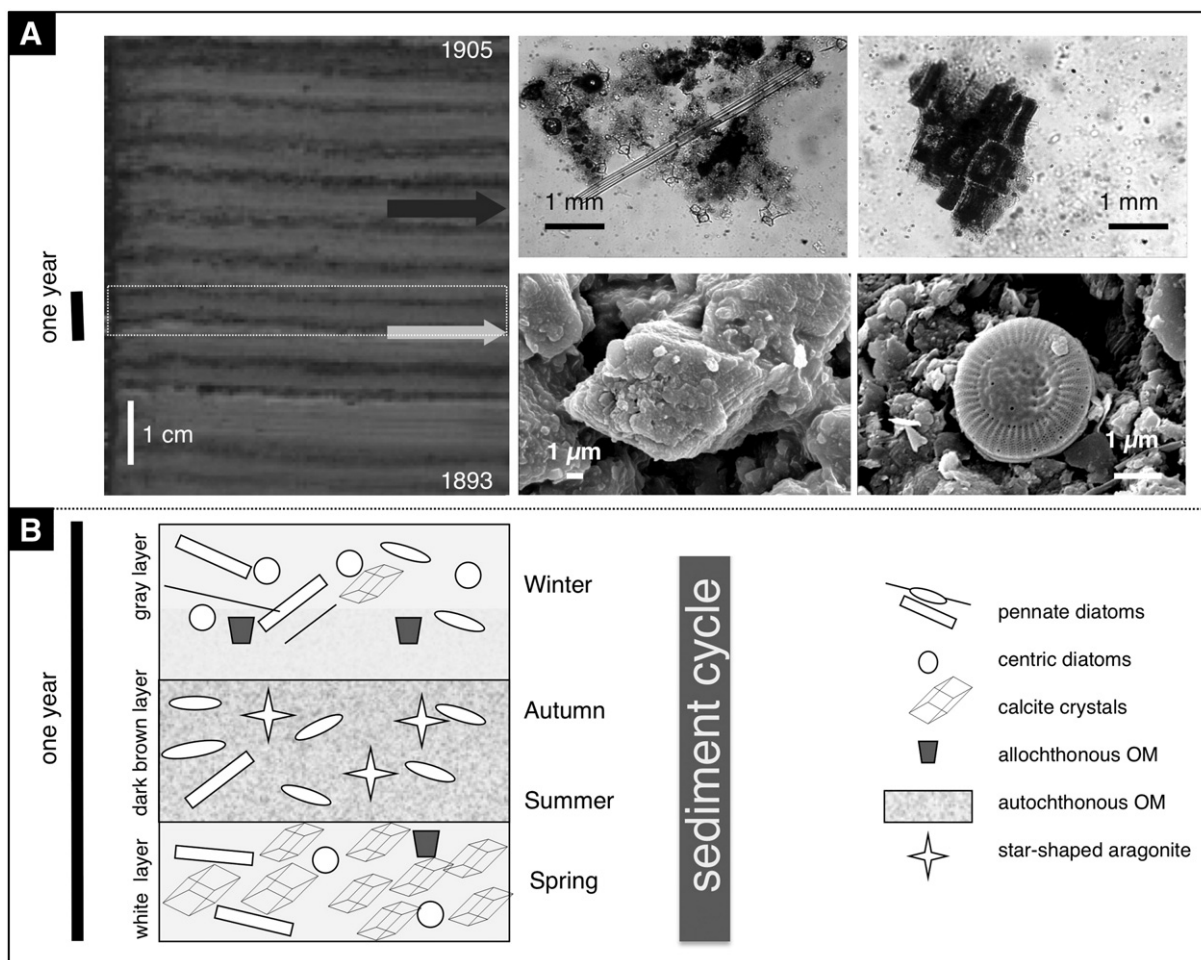


Fig. 4. (A) High-resolution core photograph showing a detail of a laminated section deposited between 1893 and 1905 AD. The main components of each lamina are shown in two photographs of smear slides of amorphous and refractive organic matter (top left and right images, respectively); and SEM microphotographs displaying a crystal of an authigenic carbonate and a centric diatom (bottom left and right images, respectively). (B) Schema showing the interpreted annual cycle as recorded in each ideal varve for the most recent sediments. Notice that occasionally the white carbonate pure component is missing and the varve comprises only two laminae.

(~1 mm) are almost entirely composed of authigenic carbonate crystals and sporadic centric diatoms (Fig. 4A). Furthermore, SEM inspection of selected samples combined with X-ray diffractometry reveal that rhomboidal crystals of low-Mg calcite dominate the lowermost part of the core whereas star-shaped aragonite crystals prevail in the uppermost 26 cm. Their crystal development and association to diatom frustules indicate that these carbonates are undoubtedly of authigenic origin. The homogeneous grayish to brownish intervals that are present throughout core BU 00-2 (Fig. 3) are dominantly of detrital origin and variable thickness (132.6 to 126.2 cm; 118.2 to 108.2 cm; 83 to 63 cm; 35.9 to 31 cm), containing clay particles, diatom fragments, terrigenous organic matter, framboidal pyrite and quartz fragments. In contrast to the other homogeneous intervals, the layer between 83 and 63 cm shows some particle-size grading, with a 3-cm thick coarser section at its bottom.

4.2. Physical properties

Fig. 5 shows the physical properties of core BU 00-2, which can be considered representative of the basin general sedimentation and has been studied in detail. Bulk magnetic susceptibility is generally low but shows remarkable changes with the changed lithology in the homogeneous layers: The highest values ($\sim 30 \times 10^{-5}$ SI) are recorded at 117 cm, in concurrence with dark-colored massive layers, whereas two intervals with lower values are observed between 83 and 63 cm and at ~40 cm, respectively, coinciding with a light-colored homoge-

neous layer. The uppermost 38 cm display decreasing magnetic susceptibility upwards. The density curve shows a similar behavior, but in contrast to the magnetic signature, all four homogeneous layers are characterized by increased density values (1.4–1.6 g/cm³) compared to the low-density signature (1.1–1.3 g/cm³) of the laminated sections.

4.3. Chronology

The age of the most recent sediments was constrained using the ¹³⁷Cs gamma-counts as shown in Fig. 5. Maximum Cs activity is observed at 15.5 cm and can be assigned to the climax of atmospheric nuclear bomb testing in 1963 (Appleby, 2001). A somewhat smaller activity peak at 5.5 cm can be assigned to the 1986 Chernobyl accident. A comparison of the ¹³⁷Cs-based chronology with information gained from the visual assessment of the laminae indicates that the laminae couplets (occasionally triplets) are of annual origin (Fig. 4), signifying that the age model can be extrapolated from the upper part of the core through varve counting. A computer-assisted image analysis provided the thickness of each individual lamina and supported the established varve-based age model. Thus, once the homogeneous intervals were virtually “removed” from the record, the lamination provides a continuous, robust age model covering the last 259 years. Further support of the established age model originates from the homogeneous layers that are interpreted as earthquake-induced mass wasting events (Anselmetti et al., in prep.). The varve-based ages of these event layers fit well with historically reported

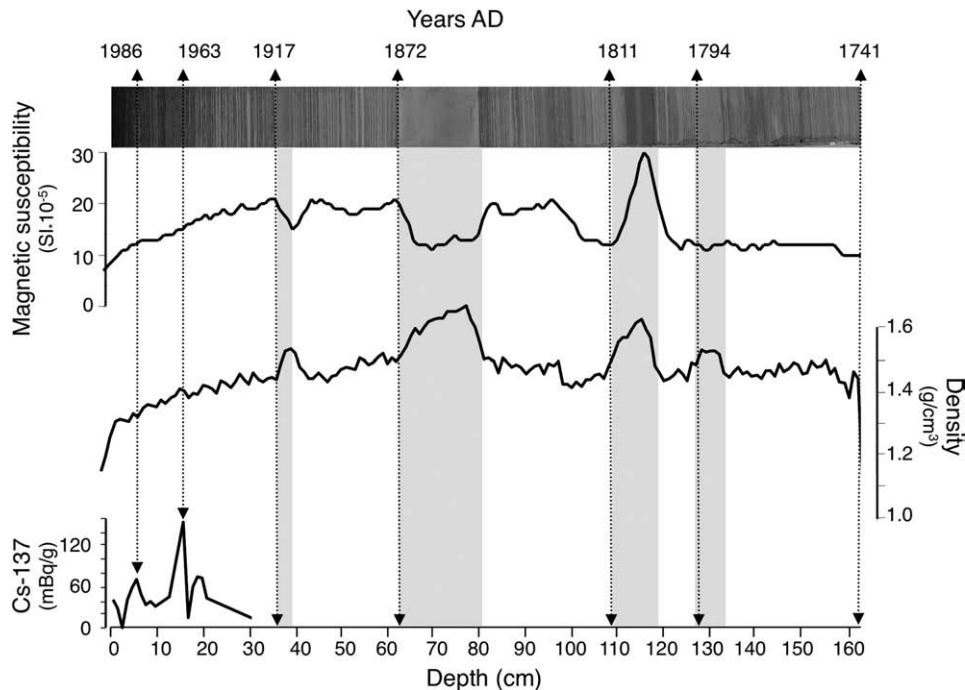


Fig. 5. High-resolution photograph of core BU 00-2 showing laminated and homogeneous (shaded) intervals. These lithological changes are very well represented in both magnetic susceptibility and sediment density that show distinctive average values. The Cs-137 profile shows the 1963 AD peak that corresponds to the pair of laminae number 37, confirming their annual character. The 1986 peak represents the Chernobyl accident.

earthquakes (1794, 1811, 1872, and 1917), reaffirming the validity of the age model used in this paper as well as the annual resolution of this sediment core.

4.4. Organic and inorganic geochemistry

Fig. 6 shows the multi-proxy geochemical record for both organic and authigenic carbonate fractions in core BU 00-2. The TOC content increases upcore, reaching almost 4% in sediment layers that correspond to the year 2000 AD. This general trend is punctuated by several intervals of substantially lower organic content (~1%) and distinctively homogeneous lithologies. Analogously, the carbon-normalized HI and OI display similar variations throughout the core. While HI varies between 65 and 200 mg Hc g⁻¹ TOC, the average value for the OI was 200 mg CO₂ g⁻¹ TOC, with peaks of up to 400 mg CO₂ g⁻¹ TOC. It has to be noted that these three parameters have been measured in the same samples strictly at 5 cm intervals, irrespective of lithological variations, while the other organic and inorganic parameters (i.e., C/N, isotopes ratios) were determined at a 10-year interval in order to avoid the homogeneous units.

The C/N ratios display relatively small interannual variations (notice scale exaggeration in Fig. 6) but a clear decreasing trend could be observed during the last 100 years, with the lowest values (~9) in the most recent sediments. Carbon and nitrogen stable isotope ratios of the bulk organic matter fraction show somewhat opposite trends from the bottom to the top, except for the uppermost ~25 cm where both parameters co-vary showing trends towards higher values. The $\delta^{13}\text{C}_{(\text{OM})}$ is about -29.0‰ in the oldest sediments compared to -26.0‰ in the most recent sediments. The $\delta^{15}\text{N}_{(\text{OM})}$ decreases from ~5.0‰ to ~3.0‰ between the bottom of the sediment core and 25 cm depth, and then increases to approximately 7.0‰ in the top of the core.

The oxygen and carbon stable isotopic composition of the authigenic carbonates show a strong covariance, with an upcore- $\delta^{18}\text{O}_{(\text{carbonate})}$ change from -7.0 to -1.0‰ and a concomitant $\delta^{13}\text{C}_{(\text{carbonate})}$ increase from ~-4.5‰ to ~2.0‰.

5. Discussion

5.1. Model of varve formation

The textural and compositional uniformity, as well as the systematic succession of the lamination, combined with the excellent correspondence between results of visual counting of the coupled or triple laminae and the ¹³⁷Cs-based chronology, provide conclusive evidence that the laminae are in fact varves *sensu strictu*.

With this certitude, our observations allow us to formulate a model of varve formation for Lake Butrint's most recent sediments, as summarized in Fig. 4B. The spring and summer period is marked by increasing temperatures in the epilimnion (Fig. 2B). The thermal stratification in concert with high nutrient concentrations at the beginning of the productive period triggers the blooms of both centric and pennate diatoms. These algal blooms, in turn, increase the pH of surface waters and thus create a chemical disequilibrium in the carbonate system resulting in the massive precipitation of carbonate and, upon sedimentation of the carbonate particles, the generation of the white lamina. This precipitation continues to some extent during summer and early fall, when a large amount of settling amorphous organic matter (AOM) is buried to yield the dark-brown lamina. These darker laminae also contain a comparatively large proportion of star-shaped aragonite crystals and pennate diatoms. The winter season is characterized by the grayish sediment laminae, predominantly containing allochthonous organic matter embedded in a dominantly detrital clay matrix (with the sporadic occurrence of diatom frustules and authigenic carbonate crystals). Although no sediment trap data are available for Lake Butrint, which would allow us to verify this sedimentation sequence of events, existing water column data are consistent with the proposed scenario. Moreover, a similar seasonal sedimentation pattern is common in many temperate lakes (e.g., Kelts and Hsü, 1978) where carbonate-rich laminae related to high-pH conditions during phytoplankton blooms characterize spring and summer sediment layers. Detritus from terrestrial sources (i.e., Vrina and Vurgus plains), and occasionally through resuspension from the littoral zone, dominate the second layer of a typical organic-rich varve

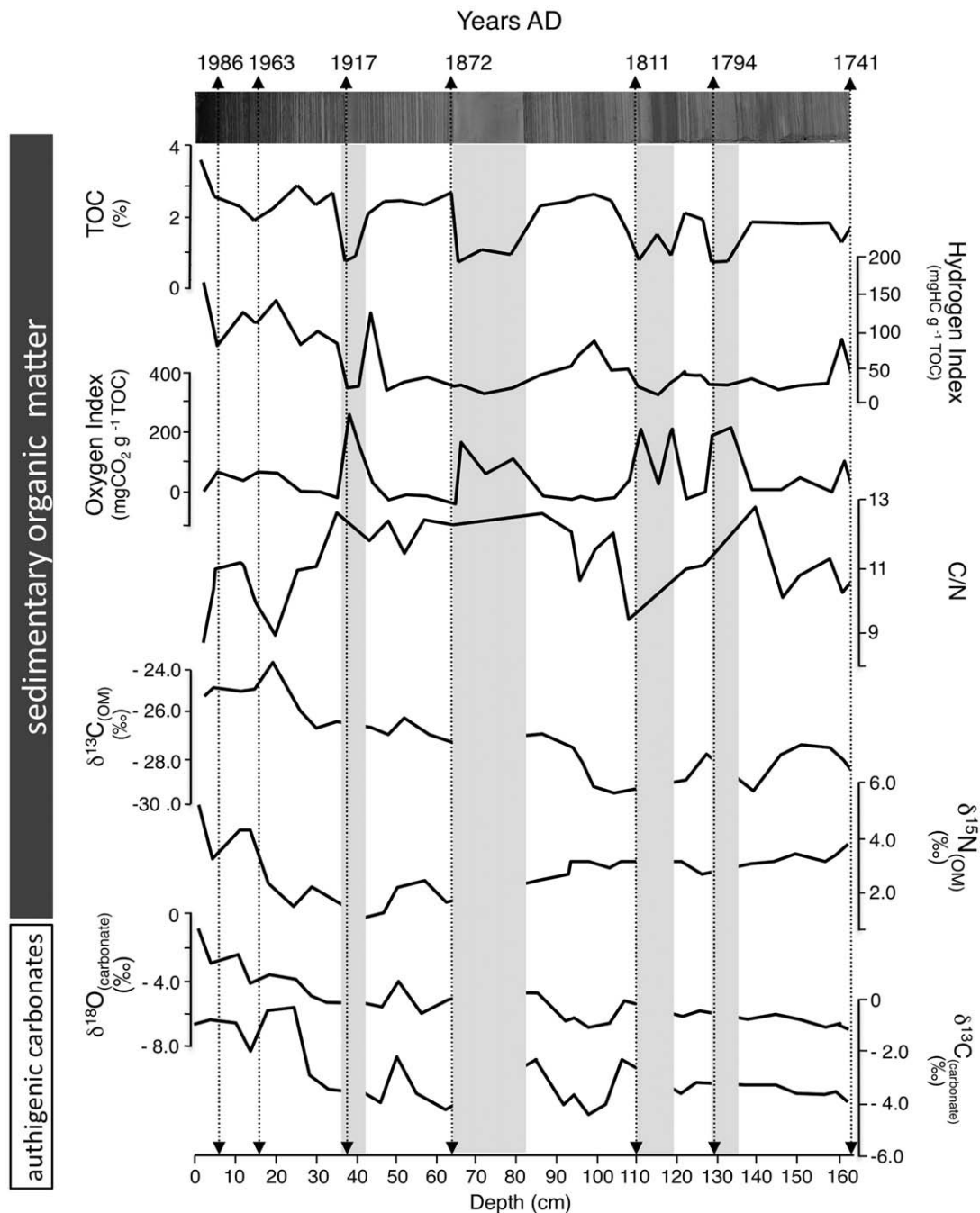


Fig. 6. Geochemical parameters measured in core BU 00-2 for both bulk organic matter and authigenic carbonate fractions.

couplet. The third component of the varve reflects periods of increased runoff in fall and winter in the Lake Butrint region, typical for a Mediterranean climate with wet winters.

5.2. Geochemical record of changing environmental conditions

The increasing TOC values towards the core top are consistent with a progressive eutrophication of the lake. This eutrophication trend is indicated in our record by an augmentation in the proportion of algal-type amorphous organic matter (AOM). Relative changes in HI can be linked to variations in the contribution of phytoplankton-produced organic matter to the bulk sediments, a good proxy for lacustrine primary productivity. The relatively low HI values are most probably related to a matrix effect due to the high carbonate content that may

act as an effective shielding of OM preventing its cracking during pyrolysis (Steinmann et al., 2003). Between the 17th century and ~1925 AD, constant HI values around 50 mgHC g⁻¹ TOC together with comparatively low C contents suggest that nutrient input and algal productivity were low. Primary production increased during the 1930s when the trophic state of the lake started to change dramatically (Negroni, 2001). High organic carbon input also occurs in 1959 and 1996 AD (Fig. 6). These three dates correspond to epochs of enhanced eutrophication of the system due to the increasing use of fertilizers and agricultural activity in the lake catchment.

The OI is essentially invariant (ca. 200 mgHC g⁻¹ TOC) during the entire studied interval, which indicates that the input of allochthonous OM to the lake has remained relatively stable. The general distribution through depth of the OI in the sedimentary core is anticorrelated to

that of TOC, the latter displaying the lowest values during mass wasting events that contain allochthonous organic matter and terrigenous material.

The overall C/N ratio indicates a prevailing AOM signature with only small variations (notice the enlarge scale in Fig. 6). The most recent sediments display a particularly dominant AOM signal (i.e., values below 10) consistent with the above-described gradual eutrophication of the lake (Tyson, 1995; Meyers and Lallier-Verges, 1999).

The changes in nitrogen isotope composition of OM are also consistent with the Rock-Eval® data confirming increased eutrophication during at least the last six decades. The increase in $\delta^{15}\text{N}_{\text{(OM)}}$ since 1946 AD can best be explained by an increase in primary productivity that is compatible with an increasing input of ^{15}N -enriched dissolved inorganic nitrogen due to expanding agricultural activities (Teranes and Bernasconi, 2000) that peaked in the early 1960s with main algal blooms that enhanced water column anoxia (Negroni, 2001). In the same line, both $\delta^{13}\text{C}_{\text{(OM)}}$ and $\delta^{13}\text{C}_{\text{(carbonate)}}$ show a consistent increasing trend from the bottom of the sediment core to the top (Fig. 6). This trend further confirms the observed enhancement of both increase in primary productivity and OM preservation (Teranes et al., 1999; Teranes and Bernasconi, 2005), as well as a decrease of the freshwater input, which provides dissolved inorganic carbon that is generally lower (average $\delta^{13}\text{C} - 5$ to -6‰) than that of marine origin (approximately 0‰).

Oxygen isotopic records of Mediterranean lakes are mostly responding to regional changes in water balance (Roberts et al., 2008). The $\delta^{18}\text{O}_{\text{(carbonate)}}$ values determined for the oldest sediments recovered in this study (1741 AD) are significantly more negative, indicating a comparatively higher freshwater input at that time that would have reduced the lake salinity and thus the O-isotope budget. This interpretation is supported by the observed decrease in the thickness of the low-Mg calcite-rich laminae (Fig. 4B) during the last phase of the Little Ice Age (LIA) recovered in the lowermost ~ 50 cm of the studied core (Fig. 6).

The carbonate O-isotopic trends in the most recent portion of the Lake Butrint sedimentary record are quite different and even reverse to those from their temperate Alpine counterparts such as Swiss Lake Baldeg (Teranes et al., 1999) and Lake Greifen (McKenzie and Hollander, 1993). The $\delta^{18}\text{O}_{\text{(carbonate)}}$ of Lake Butrint sediments display a substantial enrichment in ^{18}O during the second part of the 20th century, raising $^{18}\text{O}/^{16}\text{O}$ ratios close to values that are characteristic for marine settings (Rosen et al., 1995; Gat, 1995). These values are most likely the result of a progressive salinization of the lake, a phenomenon that is additionally reflected by gradual changes in carbonate precipitation in the lake since 1943 AD (from low-Mg calcite to aragonite) (Fig. 7). Historical data indicate that this salinization is mostly a result of anthropogenically-induced changes in the hydrological balance of the lake (Fig. 2A). The deviation of the Bistrica River to the sea in 1959 substantially diminished the freshwater input to the lake leading to an increase in salinity. This trend was further enhanced with the dredging of the Vivari Channel in 1986 and 1987, which increased the marine influence by facilitating the water exchange between Lake Butrint and the Mediterranean. Thus, enhanced inflow of Mediterranean saline waters to the lake through the Vivari Channel also contributed to the observed salinization. A re-deviation of the Bistrica River to the lake and the construction of a dam to artificially regulate the water level were accomplished in 1988. This sequence of events that produced a sensible increase in the lake salinity is documented by the positive trend in both the $\delta^{18}\text{O}_{\text{(carbonate)}}$ and $\delta^{13}\text{C}_{\text{(carbonate)}}$.

In concert with these human-triggered changes in the more local hydrology, mid-term regional changes in evaporation (E) versus precipitation (P) rates may have contributed to the observed carbonate isotope trends. Instrumental data from a meteorological station in Corfu provide evidence for an increase in the E/P ratio

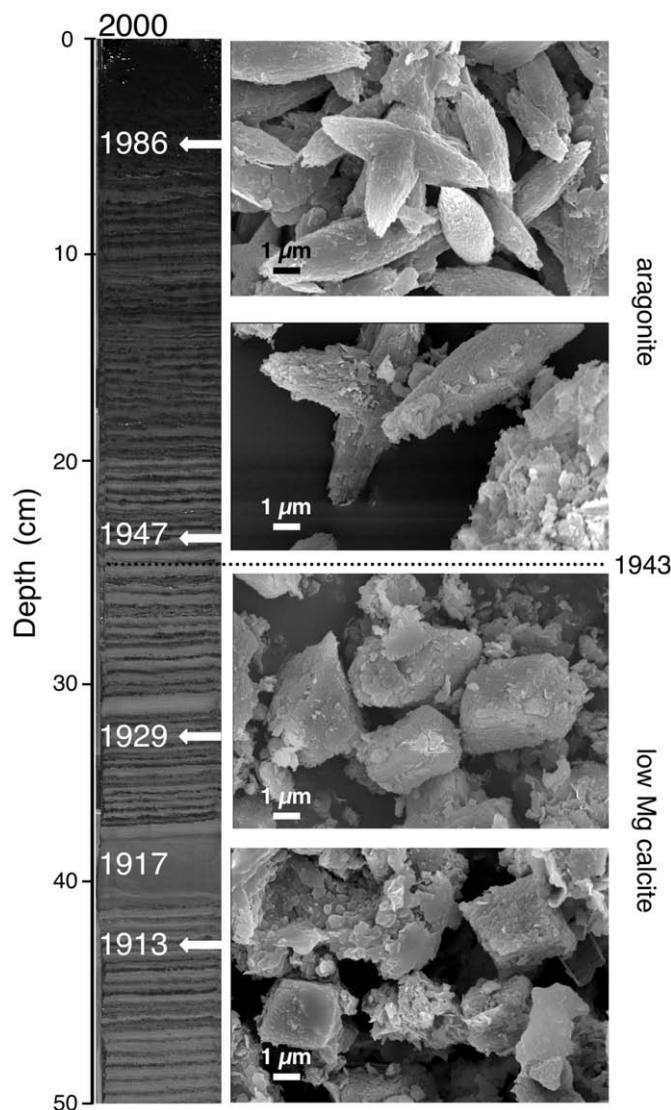


Fig. 7. Close-up photograph of the uppermost 50 cm of core BU 00-2. Selected SEM microphotographs representative of the white laminae show a sharp change in the mineralogy of the carbonates at 27 cm (i.e., 1943 AD). X-ray diffractometry analyses indicate that the lower part of the core is dominated by low-Mg calcite whereas aragonite is the prevailing carbonate in the uppermost 27 cm. White arrows indicate the position of the samples and their calendar ages.

during the second half of the last century. This change in the E/P probably stands in close association with a positive NAO index as shown in Fig. 8A. An increase in the E/P ratio in the lake Butrint region may have acted to increase the $^{18}\text{O}/^{16}\text{O}$ ratio of the lake water and thus of the carbonate minerals that have been precipitated in isotopic equilibrium with the lake, yet this mechanism alone clearly cannot be responsible for the observed O-isotope shift to marine $\delta^{18}\text{O}$ values. Time series meteorological data for Athens (Xoplaki et al., 2001) indicate a warming trend for the end of the 20th century coinciding with a positive phase of the reconstructed NAO index. Furthermore, a general trend toward a strengthening of the NAO–precipitation relationship over most of Europe has been detected for the twentieth century (Vicente-Serrano and López-Moreno, 2008). Although the isotopic signal is dominated by the human-induced salinity changes, the spectral analyses of the thickness of the detrital clay-dominated gray winter laminae over the entire core reveals prevailing frequencies that can be linked to changes in precipitation patterns (Fig. 8B). This frequency of changes has been previously connected to NAO and/or ENSO-like phenomena for other central Mediterranean lake records

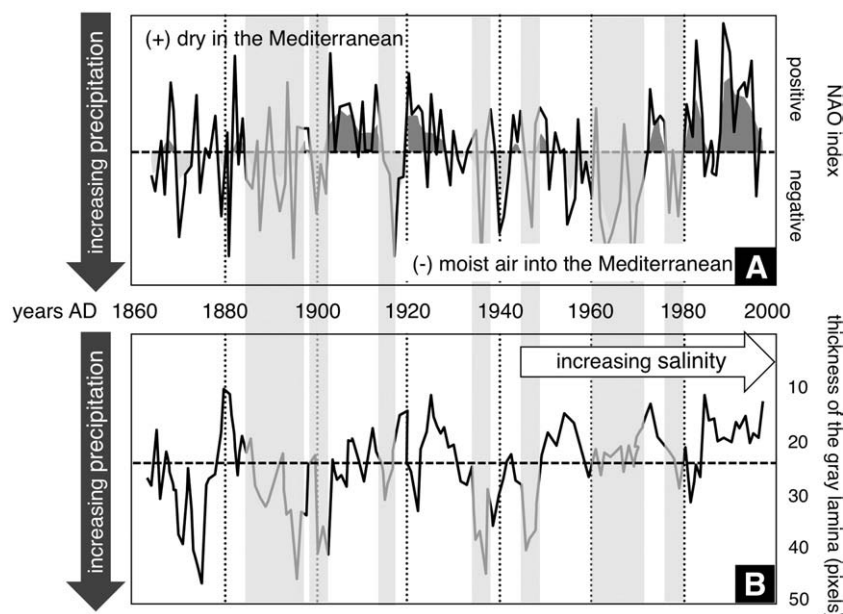


Fig. 8. (A) Reconstructed variations in the NAO index since 1860 AD, showing positive and negative phases (after www.ldeo.columbia.edu/NAO/). (B) Thickness of the gray laminae covering the same time interval. The dominant allochthonous character of these laminae indicates that they are representative of the months with higher runoff (i.e., winter rainy season) that is highly dependent on the NAO index mode.

in different time windows (Chondrogianni et al., 2004). Furthermore, image analysis of the Butrint record has demonstrated that sedimentary intervals containing thicker gray laminae (i.e., elevated precipitation rates during winter) coincide with negative phases of the NAO index (Fig. 8A and B). Since this index exhibits considerable interseasonal and interannual variability, prolonged periods (several months) of both positive and negative phases of the pattern are common within a single year. The wintertime NAO also exhibits significant multi-decadal variability partially overlapping this annual trend (Hurrell, 1995; Chelliah and Bell, 2004). The latter may explain the imperfect correlation between lamina thickness and the NAO index, as the sediments integrate the total precipitation during the winter season and, hence, average out interseasonal variations.

6. Summary and conclusions

Lake Butrint sediments of the last ~300 years are annually layered and provide thus a unique and well-dated time series to study past climatically-triggered environmental changes as well as anthropogenic impact along the coast of the Ionian Sea. The varves are composed of a white (carbonate-rich) and a dark (organic-rich) couplet, reflecting lake water chemistry, evaporation and biologic productivity from spring to fall, and a grey detrital-dominated clay layer, reflecting precipitation and runoff conditions in winter.

The multi-proxy dataset for the laminated sediments of Lake Butrint revealed clear eutrophication and salinization trends during the 20th century. Relevant human activities that lead to the observed trends, include the increasing use of fertilizers and more intensive agriculture, changes in the irrigation network that have substantially diminished the flow of freshwater into the lake and/or increased the exchange with saline water sources, and expanding human settlements around the lake and in the catchment, leading to enhanced groundwater consumption and pollutants/nutrients delivery to the lake basin. As a result of the eutrophication, the lake experienced anoxic crises (e.g., 1987 AD) with dramatic consequences for the biodiversity and the ecosystem (Negroni, 2001).

We also observed an interdecadal cyclicity in the varves thickness with dominant frequencies around four years suggesting that the sedimentological and geochemical records are at least partially controlled by the NAO and/or ENSO-like phenomena. While our data

show that the anthropogenic impact on Lake Butrint during the last half of the 20th century played a fundamental role in changing the isotopic composition of authigenic carbonates, it seems, that (given the good correlation between the sedimentary record of precipitation and the NAO index (Fig. 8)) this historically-documented human occupation in the catchment only partially masked the climate record of Lake Butrint sediments. Thus, we were able to demonstrate that the integration of microstratigraphic and stable isotopic results from this study allowed us to disentangle human and climatically-induced environmental changes in Lake Butrint.

This study should be motivation for future work. We anticipate that long sediment cores from Lake Butrint will provide potentially varved sections, which will permit the reconstruction of environmental change and historic anthropogenic impacts, during at least the late Holocene period at high temporal resolution. The sedimentary archive of Lake Butrint may, hence, offer new insights into human activities and perturbations during the ancient Greek and Roman periods and their influence on coastal lacustrine deposits.

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