$\delta^{15}N$, $\delta^{18}O$ and $\delta^{13}C$ isotopes in sedimentary material from Dispilio excavation, north Greece

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Abstract. Lacustrine sediments retain organic and inorganic components presenting valuable information regarding the past climate variations in lake basins as well as the present conditions. Soil samples, that referred to Dispilio excavation were subjected to stable isotope analysis ($\delta^{18}O$, $\delta^{13}C$, $\delta^{15}N$) trying to assess paleoclimatic information. $\delta^{18}O$ and $\delta^{13}C$ exhibited an excellent correlation typical for closed basins and long residence-time lakes. No isotopic disequilibrium events detected allowing a paleoclimatic interpretation. Two trends distinguished in soil core. The one concerns the lower part (1.00-2.00m) with enriched mean $\delta^{18}O$ values highlighting a cooler and drier environment. The upper part (0.40-0.80m) exhibits depleted $\delta^{18}O$ values highlighting a warmer and wetter environment. A runoff episode detected in the upper zone probably enhanced by deforestation events. This is consistence with the ^{14}C order of Early/Middle Bronze age where an intense human activity has been reported.

Keywords: isotopes, sediment, Dispilio, Kastoria

1. Introduction

^{18}O, ^{13}C, and ^{15}N isotopes are commonly applied in paleolimnology studies to fingerprint lake processes (such as organic production, mixing or residence time) related to paleoclimate records. The formation of calcium carbonate depends on the concentration of bicarbonate of calcium ions in water and is characterized by the following reaction: $Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3(s) + H_2O + CO_2$. The main factor that controls the carbonate precipitation is the intake of CO_2 during photosynthesis process from aquatic macrophytes and phytoplankton. In lakes of temperate and high latitude, carbonates produced mainly during the summer months and maximum primary productivity periods. $\delta^{18}O$ of lacustrine sediments mainly depends on isotopic composition of the lake water and the water temperature when the carbonates precipitate. Both factors are intimately linked to the climatic conditions. Light isotopes (^{16}O) transferred to vapor phase leaving heavier oxygen isotopes (^{18}O) in water reservoir. Therefore, variations in $\delta^{18}O$ of lacustrine carbonates are interpreted as changes in the ratio precipitation / evaporation (Siegenthaler and Oeschger 1980). These interpretations based on the assumption that in lake systems the calcite precipitates in known isotopic equilibrium (Epstein *et al.*, 1953; Friedman and O'Neil, 1977).

2. Material and Methods

Soil samples, that referred to Dispilio excavation core (2.00m) with sample step 0.20m, were subjected to stable isotope analysis ($\delta^{18}O$, $\delta^{13}C$, $\delta^{15}N$) at the Laboratory of Stable Isotopes and Radiocarbon, INN, NCSR Demokritos, Greece, trying to assess paleoclimatic information. Carbon and oxygen stable isotopes were analyzed with a ThermoScientific Delta V Plus mass spectrometer (GasBench II device) while nitrogen isotopes were analyzed with a continuous-flow isotope ratio-monitoring mass-spectrometer (Flash Elemental Analyzer coupled with Delta V Plus Isotope Ratio Mass Spectrometer). Repeated measurements took place for each sample. Analytical precision was ±0.1‰ for $\delta^{13}C$, ±0.2‰ for $\delta^{18}O$ $\delta^{15}N$.

3. Results and Discussion

Dispilio settlement located S-SW from Kastoria Lake. This polymictic lake, with long water retention time, founded at 630m a.s.l., with max and mean depth around 8m and 4m respectively. Kastoria Lake basin exhibits mean annual temperature 12.5^oC. Mean maximum values reported on July and August (22.8°C and 22.9°C respectively) while mean minimum values reported on January (2.4°C). Moreover, mean precipitation $\delta^{18}O_w$ values range between -9.5‰ and -8.6‰ VSMOW (Dotsika *et al.*, 2010) in Kastoria Lake basin while in Dispilio area mean $\delta^{18}O_w$ value is about -8.5‰ VSMOW. Based on the aforementioned, the proposed equations by Hays and Grossman 1991 [$T^oC=15.7-4.36(\delta_c-\delta_w) + 0.12(\delta_c-\delta_w)2$ eq. (1)] and the fraction factor between carbonate and precipitation ~ -0.24‰ (Hays and Grossman, 1991), the resulted $\delta^{18}O_c$ values of modern calcite that precipitates in Kastoria Lake basin range between 26.204‰ and 27.104‰ VSMOW. Using the equation $\delta^{18}O_{V\text{-}SMOW}$=1.03091*$\delta^{18}O_{V\text{-}PDB}$+30.91 [eq. (2)] that reported by Coplen *et al.*, (1983); Coplen (1996); Hoefs (2007) the converted modern calcite $\delta^{18}O_c$ values ranged between -4.56‰ and -3.69‰ PDB.

$\delta^{15}N$, $\delta^{18}O$ and $\delta^{13}C$ values in bulk soil samples from Dispilio excavation ranged from 5.3‰ to 9.5‰ AIR (mean value 7.4‰), from -12.5‰ to -5.6‰ PDB (mean value -8.5‰) and from -21.7‰ to -9.1‰ PDB (mean value -13‰) respectively. The factors that control the isotopic signals in lacustrine sediments are bulk carbonates with different origin particles, the hydrological regime and water temperature under which the calcite precipitates, and finally the biological activity that influence the carbonate chemistry. $\delta^{18}O$ and $\delta^{13}C$ exhibited an excellent correlation (r^2=0.83). This correlation is typical for closed basins and long residence-time lakes (Li and Ku 1997). The factors that control at the same time $\delta^{18}O$ and $\delta^{13}C$ of lake water, and therefore sediments are the changes in the water balance, i.e. the ratio of precipitation / evaporation. In turn these patterns are determined by the circulation of air masses. Therefore, the reduction in precipitation height will result in strong evaporation and finally to more positive $\delta^{18}O$ values. The smaller the lake basin the more sensitive to isotopic equilibrium with basin environment. Therefore, closed basins present repeated cycles with more positive $\delta^{18}O$ values, highlight drier periods, and negative $\delta^{18}O$ values, for wetter periods (Talbot and Kelts, 1990). Consequently, begging from the end of soil core, the soil zones 1.00m-2.00m, 0.40m-0.80m, reflect the passage to from drier to wetter conditions alternately (Figure 1). The $\delta^{18}O$ isotopic variation align with the reported morphological comments (Karkanas, P., 2002) where soil layer 2.00-1.80m reflects a riparian environment of high energy with strong waves and currents in direct interaction with the lake, soil layer 1.80-1.00 characterized by alternating deposits from wavy to stagnant water and soil layer 1.00-0.40m corresponds to an environment without strong interaction with lake water except wet periods. Additionally, soil layer 1.80-1.00 reflects environments of undisturbed lakes, rich in reeds. This picture match with the modern one in front of the excavation site (Chatzitoulousis, S. 2008). The interaction with the well mixed open lake and natural deposits, enriches the soil with large amounts of silicon allowing the high biological activity. This organic load together with the undisturbed environment enhance the diatom growth (Chantzi *et al.*, 2016). Soil layers of 0.40m, 0.60m, 1.20m, 1.40m and 2.00m exhibit stable $\delta^{18}O$ values about -8‰ PDB (Figure 1) while $\delta^{13}C$ values range between -15.9‰ PDB to -10.4‰ PDB. These $\delta^{18}O$ and $\delta^{13}C$ values are typical for soil calcites where the less negative values result to stronger evaporation and/or reduced precipitations. Soil layers of 0.20m (sample Sc_1) and 0.80m (sample Sc_4) excluded as isotope values reflect different episodes. Detailed, soil layer 0.20m presents $\delta^{18}O$ value about -5.6‰ PDB much more positive compared to other layers and closer to the of modern precipitated calcite (estimated -4.56‰ and -3.69‰ PDB). The fact that soil layer reflects only 20cm from the surface justifies the influence of modern calcite precipitation as drains runoff. Moreover, maximum $\delta^{15}N$ values presented on 0.20m layer. This is consistence with elevated NO_3^- values in the riparian zone ranging from 2.3mg/l to 20.7mg/l highlighting a modern pollution. Soil layer 0.80m (sample Sc_4) presents a much more negative $\delta^{18}O$ value about -12.5‰ with respect to rest soil layers, accompanied by much more negative $\delta^{13}C$ value -21.7 ‰. However, $\delta^{15}N$ do not follow this trend of depleted values. In fact, excluding 0.80m layer, $\delta^{15}N$ and $\delta^{13}C$ values exhibit a good correlation (r^2=0.63). This implies that carbon formation in 0.80m soil layer is gathered by different conditions.

Carbon isotopes values in sediments controlled by terrestrial process of lake basin and within the lake. The first concerns the particulate organic carbon (POC) which accumulates into the lake as a runoff result. The pattern of POC $\delta^{13}C$ values depends on the concentration of CO_2 in soil where the concentration is a function of soil temperature and moisture content (Dorr & Mi nnich 1987). Autochthonous processes concern dissolved inorganic carbon (DIC) absorbed by algae produced within the lake. $\delta^{13}C$ values in DIC material related to atmospheric CO_2, calcareous bedrock and fractionation factor of lake (Diefendorf *et al*. 2008). A major shift to negative $\delta^{13}C$ values could be justified by biogenic methane formed in anaerobic lake sediments (Whiticar 1999). Usually, anaerobic conditions accompanied by eutrophication conditions where calcite precipitation occurs under isotopic disequilibrium resulting in more negative $\delta^{18}O$ values. Gat and Lister (1995) have reported that eutrophication episodes have an impact on oxygen isotope values. However, if the notable negative shift of $\delta^{18}O$ and $\delta^{13}C$ values in 0.80m zone gathered by eutrophication events this impact should be evident on $\delta^{15}N$ values. The $\delta^{15}N$ signal of organic matter is ordered by the available nitrogen sources to the organism either within the lake or sourced by the lake basin. Atmospheric, methanogenic or nitrate origin result in a range of $\delta^{15}N$ values that characterizes each process i.e. N_2 ($\delta^{15}N$ ~ 0%), NH_4^+ ($\delta^{15}N$ = -10 to 0%), and NO_3^- ($\delta^{15}N$ = -4 to 25%) (Cravotta 1997). In contrast in 0.80m layer $\delta^{15}N$ values shifted to more positive values rejecting any NH_4^+ fingerprint. On the other hand, higher lake lever or extended runoff due to deforestation supply the lake with soil material enriched in $\delta^{15}N$ values. Talbot and Lærdal, 2000 reported that episodes like this result to transient changes with a small scale increased-decreased $\delta^{15}N$ pattern. This pattern is consistent with the soil zone 0.20m-0.80m which reflects the Early/Middle Bronze age where an intense human activity has been reported (Kouli *et al*., 2007).

Based on the above, $\delta^{18}O$ and $\delta^{13}C$ values seem to controlled by climatic factors and the origin (autochthonous/terrestrial) of bulk carbonates particles, respectively. As no isotopic disequilibrium events have been detected, $\delta^{18}O$ values variety could reflect a temperature variation. The temperature of water at the epilimnion zone, upper part of lake water, exhibit temperature that reflect the mean air temperature which affect the $\delta^{18}O$ sign of precipitated calcite (Livingstone and Lotter, 1999). Considering the positive correlation between air temperature and $\delta^{18}O$ of precipitation (Kohn and Welker, 2005), the conceptual sequence is that the increase in mean air temperature would result to enriched $\delta^{18}O$ values of lake water. In turn, the enriched $\delta^{18}O$ values of lake water would result to decreased $\delta^{18}O$ values of precipitated calcite due to the fractionation between water and calcite that functions inversely (calcite decreases with increasing temperature) (Kim and O'Neil, 1997). Finally, it is concluded that two trends are distinguished in sediment core from Dispilio excavation, excluding the layer 0.20m as it is affected by modern pollution. The first trend concerns the lower part of sediment 1.00-2.00m where higher mean $\delta^{18}O$ values (-8.5‰ PDB) of precipitated calcite reflect cooler conditions and lower mean $\delta^{15}N$ values reflect reduced organic load. On the other hand, the upper layer 0.40-0.80m exhibits lower mean $\delta^{18}O$ values (-9.6‰ PDB) of precipitated calcite reflecting warmer conditions and lower mean $\delta^{15}N$ values reflecting elevated organic load. Generally, the isotopic composition of $\delta^{15}N$ in soil depends on the climatic and geographical conditions (Heaton, 1986), but agricultural practices such as fertilization, have a strong effect. The application of organic fertilizers or intensive agriculture leads to increased soil $\delta^{15}N$ values and consequently to increased $\delta^{15}N$ values in plants. The observed positive shift from the lower to the upper zone, probably reflects the transition to more organized farming practices with intense use of exogenous nitrogen sources. This is consistence with the ^{14}C order as this positive shift, with respect to $\delta^{15}N$ values, coincides with the transition from Late Neolithic to Bronze age and the reported upgrade agriculture practices (Papathanasiou and Richards, 2015). $\delta^{13}C$ values do not directly reflect climate change but support $\delta^{18}O$ interpretation by detecting episodes that affect isotope signal under disequilibrium conditions. Regarding Dispilio excavation $\delta^{13}C$ values of 0.80m soil zone reflect a soil load due to a runoff episode as probably enhanced by deforestation events.

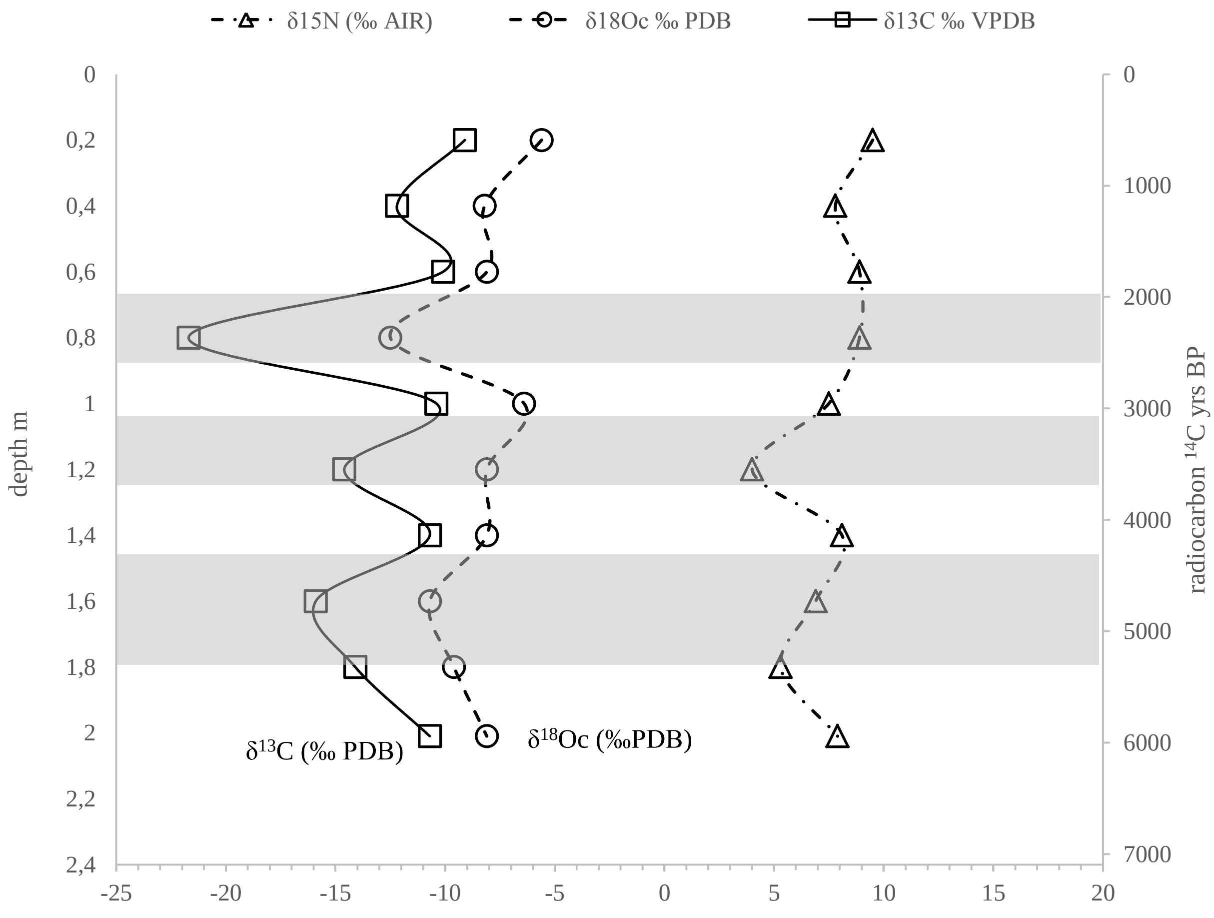

Figure 1. Stratigraphic analysis of isotopic $\delta^{15}N$, $\delta^{18}O$ and $\delta^{13}C$ values of the soil from Dispilio excavation

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