



Termination of Little Ice Age in Northeastern Anatolia: A Multi-proxy Paleolimnology Study of Lake Aygır Sediments, (Kars, NE Anatolia)

Kuzeydoğu Anadolu'da Küçük Buzul Çağının Sonu: Aygır Gölü Sedimanlarının Çoklu Proksi Paleo-Limnolojik İncelemesi (Kars, KD Anadolu)

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Abstract: Sedimentary, geochemical and stable isotope analyses of a sediment core (core AY) recovered from Lake Aygır (NE Anatolia) provide evidence of the climatic shifts during the last ~500 yrs. Sediments in Lake Aygır are composed of silty clay with a modeled ~0.16 cm/yr sedimentation rate. Multi-proxy analyses of the downcore distribution of detritally-deposited proxy elements, total calcium carbonate, organic carbon and stable isotopes reveal climatic records of the Industrial Epoch (IE; 18th-19th centuries) and the termination of the Little Ice Age (LIA; AD 1350 to 1850), represented by fluctuating Total Organic Carbon (TOC), Ca, Sr and relatively low detrital precursors (Fe, Ti, K, Rb, Zr), indicating low chemical weathering and dry conditions. The upper part of the core (192 cal yrs BP to present), identified with high detrital input, contains an increasing trend of Fe, Ti, K, Rb, and Zr together with high $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, indicating warmer conditions during the IE.

Keywords: Lake Aygır, NE Anatolia, paleoclimate, sediment coring, stable isotope.

Öz: Aygır Gölü'nden (KD Anadolu) alınan sediman karotunun (AY karotu) sedimentolojik, jeokimyasal ve duraylı izotop analizleri son ~500 yıldaki iklim değişikliklerin kanıtlarını ortaya koymaktadır. Siltli kilden oluşan Aygır Gölü sedimanlarının modellenen sedimentasyon hızı ~0,16 cm/yıldır. Detritik olarak çökelmiş proksi elementlerin tabandan yüzeye dağılımına göre yapılan çoklu proksi analizlerine göre, toplam kalsiyum karbonat, organik karbon ve duraylı izotop verileri Küçük Buzul Çağının (KBÇ; 1350-1850 MS) Endüstriyel Dönem'e (ED, 18-19 yy) geçişini temsil eder ve bu dönem düşük ayırtma hızı ve kurak koşulları açıklayacak şekilde toplam organik karbon, Ca, Sr değerlerindeki düşüşle temsil edilir. Karotun üst kısımları ise (192 yıl öncesinden günümüze) kırıntılardaki artış ve yüksek Fe, Ti, K, Rb ve Zr konsantrasyonları yanı sıra yüksek $\delta^{18}\text{O}$ ve $\delta^{13}\text{C}$ değerleri ile temsil edilir ve Endüstri Çağının sıcak koşullarını açıklar.

Anahtar Kelimeler: Aygır Gölü, duraylı izotop, Kuzeydoğu Anadolu, paleoklim, sediman karotu.

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INTRODUCTION

Multi-proxy-based paleolimnological imprints of lake sediments provide an insight into periodic changes in climate and associated shifts in the rate of rock weathering and sediment drift around the vicinity of lakes. In line with growing interest in the sedimentary record of lakes, the fingerprints of climatic changes in Anatolian lakes during the Late Quaternary have been addressed, such as in the lakes Tecer (Kuzucuoğlu et al., 2011), Sünnet (Ocakoğlu et al., 2013), Sapanca (Leroy et al., 2010), Eske Acıgöl (Roberts et al., 2001; Jones & Roberts, 2008), Nar (Jones et al., 2006; England et al., 2008) and Gölhisar (Eastwood et al., 2007). Moreover, similar studies that determine the LIA have taken place in Poland (Gaśiorowski & Sienkiewicz, 2010), Taiwan (Wang et al., 2013), and Iceland (Ogilvie & Jónsson 2001). Paleoclimate studies accentuating the downcore distribution of proxy elements of detrital and authigenic origin have increased recently, such as in case studies of the lakes Küçükçekmece (Akçer Ön et al., 2011), İznik (Ülgen et al., 2012), Hazar (Eriş, 2013; Eriş et al., 2018) and Van (Çağatay et al., 2014; Litt et al., 2014). Besides this, proxy elements are used to shed light on rational trends inferred from the ratios of Ca/Fe and Ca/Ti (Roeser et al., 2012; Çağatay et al., 2014; 2019) as well as Rb/Sr values (Erginal et al., 2019) and Mo/Al (Kükurer, 2018), allowing assessment of the climatically-controlled deposition of lake sediments over a certain period of time.

Results obtained from Lake Aygır were previously discussed by Kükurer (2018) in terms of ecological and toxic risk assessment of heavy metals. In this study, we provide a different perspective to indicate the most recent Holocene climatic changes by using multi-proxy parameters. Therefore, we demonstrate the climatic precursors of the LIA-IE transition in terms of geochemical aspects of the sediment core. On the basis of analyses of the downcore distribution of detritally-deposited proxy elements (Fe, Ti, Rb, Sr, Zr, K), as well as the content of total calcium carbonate, organic carbon and stable isotopes ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$)

, we provide a better understanding of the termination of the Little Ice Age and a comparison with other Anatolian lakes regarding the near-bottom sediments of Lake Aygır.

STUDY AREA

Lake Aygır, a volcanic barrier lake with a maximum depth of 30 meters, is located on the Erzurum-Kars-Ardahan Plateau in the Susuz district of Kars province (Figure 1 & 2). The lake has a surface area of 4.02 km² and is 2131 m above sea level. It has a length of 3.11 km and a width of 1.86 km (Figure 1 & 2). West of the lake consists of Upper Miocene-Pliocene volcanics and Pliocene andesites and pyroclastics (Deveciler et al., 1990; Aktimur et al., 1992; Rolland, 2017). According to the data of Susuz meteorology station, located 10 km east of the lake, the average temperature in the field is 4.9 °C. The total annual precipitation average is 483 mm, and depending on convectional air currents, the maximum precipitation falls in summer. Winter precipitation is in the form of snow, which covers the ground for about 4 months.

MATERIALS and METHODS

Sampling and analyses

Using a Kajak Sediment Core Sampler with 6 cm-diameter sampling tube, a 66 cm short core was recovered at 4 m water depth in the central part of the lake for multi-proxy analyses and dating (see also Kükurer, 2018) (Figs. 1,2). Preliminary results from the core have been published by Kükurer (2018), containing an ecological and toxic risk assessment of heavy metals in Lake Aygır sediments. The same sediment samples were used in this study to evaluate the most recent climatic changes. Using a Scheibler calcimeter, the CaCO₃ content of pulverized subsamples with a weight of 0.5 gr was determined (Schlichting & Blume, 1996). The TOC within another set of pulverized dry subsamples (about 0.2-0.5 gr) was measured using the modified Walkley-Black Titration Method (Gaudette et al., 1974).

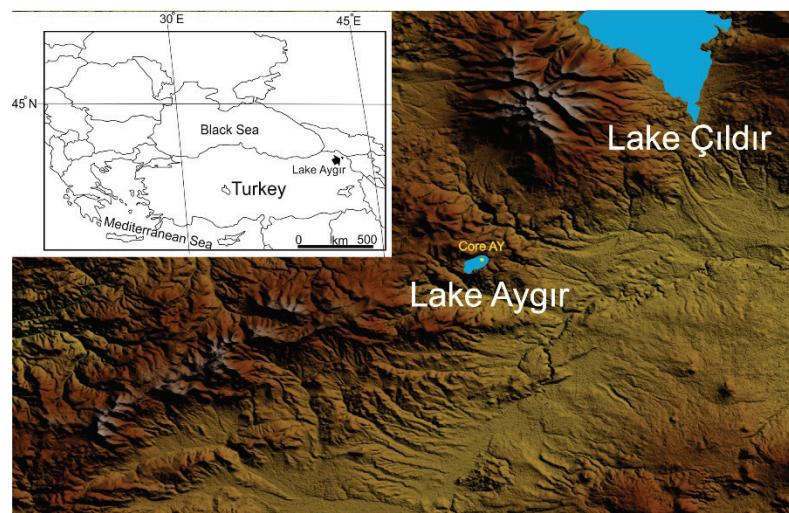


Figure 1. Location of Lake Aygır.

Şekil 1. Aygır Gölü'nün konumu.

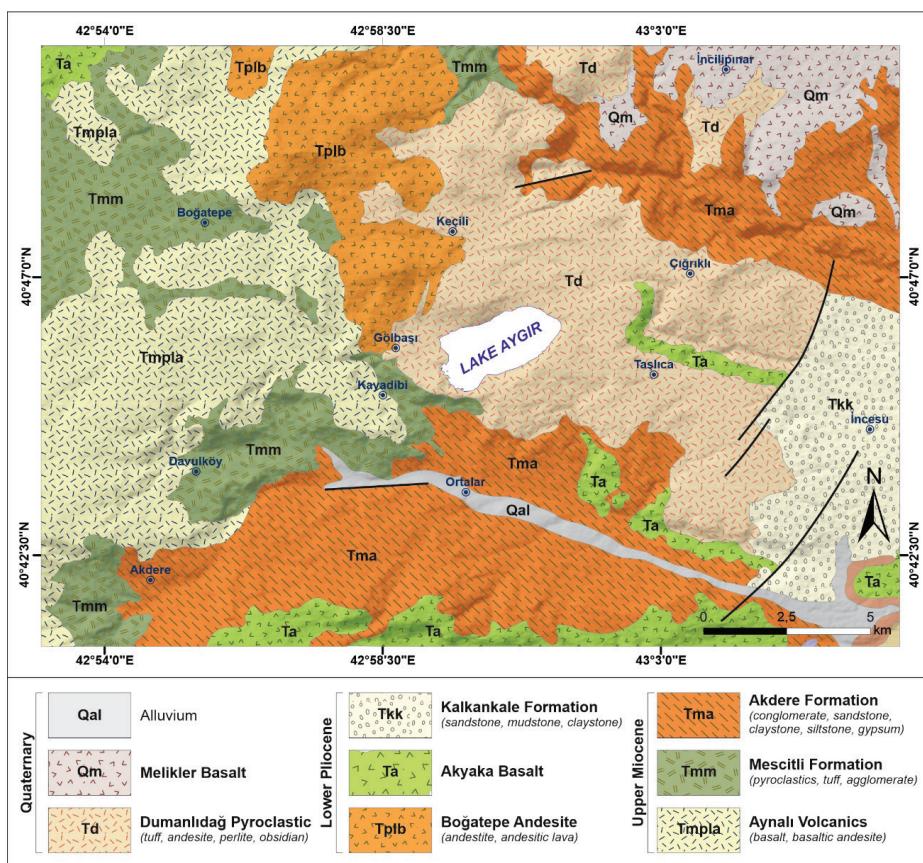


Figure 2. Geological map of the region (Aktimur et al., 1992). Note that Lake Aygır is surrounded by mainly volcanic and pyroclastic rocks.

Şekil 2. Bölgenin jeoloji haritası (Aktimur vd., 1992). Aygır Gölü genelde volkanik ve piroklastik kayaçlarla çevrilidir.

Stable oxygen and carbon isotope analyses of 33 samples were carried out in the Environmental Isotope Laboratory of the University of Arizona. For this end, carbonates of 0.5 gr sub-samples split at 1 mm were used. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of carbonates were measured using an automated carbonate preparation device (KIEL-III) coupled to a gas-ratio mass spectrometer (Finnigan MAT 252). Powdered samples were reacted with dehydrated phosphoric acid under a vacuum at 70 °C. The isotope ratio measurement was calibrated based on repeated measurements of NBS-19 and NBS-18 and the precision was $\pm 0.10\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.08\text{‰}$ for $\delta^{13}\text{C}$ (1 sigma). The isotope values obtained are reported on the Vienna-Pee Dee Belemnite scale.

Accelerated Mass Spectrometry (AMS) radiocarbon dating of bulk organic carbon within the sample taken from 66 cm depth was carried out at Beta Analytic, Miami, USA. The acquired sample showed no diagenesis of reworking. According to the 2 sigma calibrated radiocarbon outcome, the 65 cm of core sediment was dated to cal yrs BP 505 to 425. The AMS ^{14}C result was calibrated by using Calib v7.1 software (Stuvier & Reimer, 1993) with an IntCal20. ^{14}C calibration curve. The age-depth model of the studied core was produced by using an AMS ^{14}C result (Figure 3). Recovery of the core was executed by using the gravity coring system. Therefore, the top of the core represents the most recent sedimentation. The age-depth model was produced by “clam” script on the R-studio platform (Blaauw, 2010). The constructed age-depth model has non-Bayesian, linear interpolated age-depth iterations, which were calculated at 95% Gaussian confidence interval.

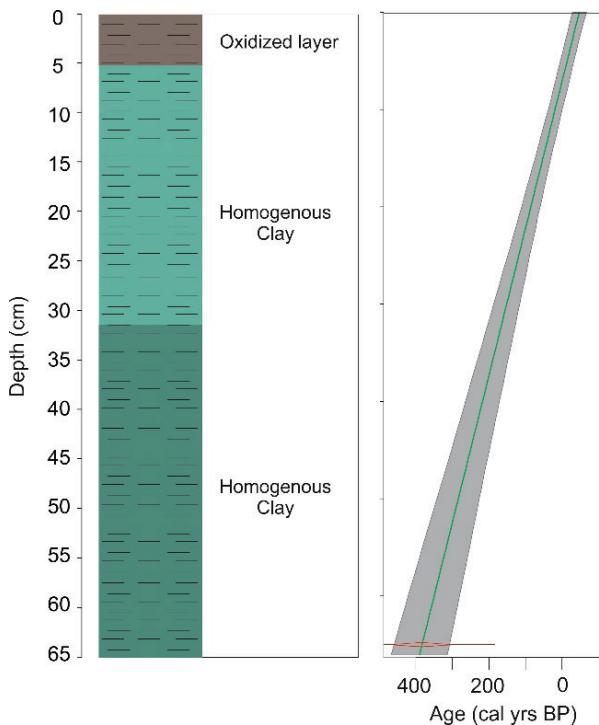


Figure 3. a) Lithology and **b)** age-depth model of studied core.

Sekil 3. a) Litoloji ve **b)** Çalışılan karotunun derinlik-yaş modeli.

RESULTS

Down-core distribution of the physical and chemical proxy data obtained from the Lake Aygır sediments allowed us to distinguish specific periods in terms of paleoclimatic records. In terms of organic carbon and calcium carbonate distribution in the studied core, a negative correlation exists. The CaCO_3 distribution shows oscillation at depths between 66 cm and 46 cm and the values tend to increase with a seesaw pattern upward ($r^2: 0.16$). However, the CaCO_3 reaching the maximum value of 94.3% in the 42-44 cm sampling interval shows a rapid decrease from this point to a depth of 34 cm and the amount of CaCO_3 decreases to 1.22% ($r^2: 0.90$). There is a regular increase in the amount of CaCO_3 from 34-36 cm deep to the surface ($r^2: 0.80$). Accordingly, the sampling level of 44 cm clearly represents the onset of a strong arid period.

The TOC concentration shows a progressive decrease up to a depth of 38 cm from the surface, beside an abnormal increase at near surface depth (0-4 cm), associated with recent anthropogenic inputs.

The oxygen and carbon isotope profiles also show two major trends. From the bottom to the sampling interval of 36-38 cm, the isotope curve is slightly oscillating in keeping with the CaCO_3 and the maximum and minimum values for $\delta^{13}\text{C}$ are 5.31 ‰ and 4.72 ‰ (V-PDB), respectively. From this depth, however, both values are 4.36 ‰ and 3.49 ‰ (V-PDB). Similarly, the $\delta^{18}\text{O}$ values range from -0.72 ‰ to 0.12 ‰ (V-PDB) below the sampling depth of 36 cm. From this depth, the maximum and minimum values for $\delta^{18}\text{O}$ are -0.1 ‰ and -1.51 ‰ (V-PDB), respectively. On the other hand, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values demonstrate a decreasing trend from bottom to top ($r^2=0.72$ and 0.65, respectively). The tendency to decrease towards the surface is more pronounced from a depth of 40 cm.

The downcore distribution of proxy elements is also indicative of climatic changes during the deposition period. At the lowermost parts of the core between 65 and 55 cm, the detrital proxies (Rb, Zr, Ti, K, Fe) display a decreasing trend in contrast to Ca and Sr (Figure 4). The organic productivity can be established by correlating Ca and Sr values as well as the organic carbon distribution. At depths between 55-46 cm, detrital proxies have a gentle positive anomaly whereas Ca and Sr levels appear to be stable (Figure 4). Organic content along with the Ca and Sr values display a similar trend in the interval between 46-35 cm. Detrital inputs are most likely decreasing during this interval. The 35-30 cm interval shows a critical change in terms of core geochemical properties, where all detrital proxies start to increase at this key level. In the rest of the core, organic content proxies (Ca and Sr) exhibit a stable trend. However, there is a considerable growth in the amount of Fe, K, Ti, Rb and Zr in this interval up to 5 cm. The uppermost part of the core (5-0 cm) shows a decreasing trend in terms of all geochemical proxies due to water saturation of the upper sediments.

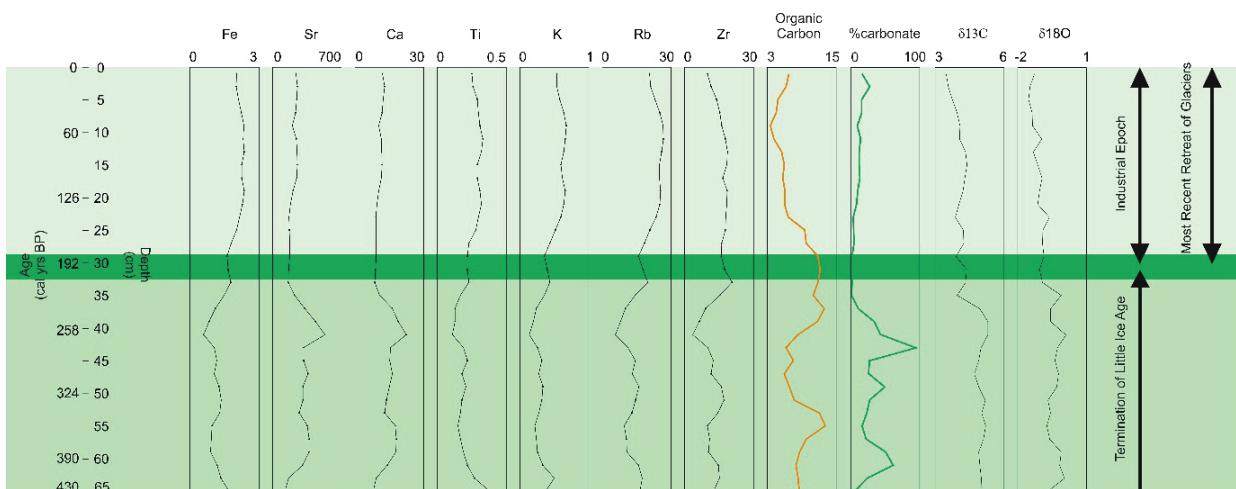


Figure 4. Downcore chemical and isotope parameter distributions. Fe, Ti, organic carbon and calcium carbonate data were obtained from Kükrer (2018).

Şekil 4. Karot boyunca kimyasal ve izotop parametrelerinin dağılımı. Fe, Ti, organic karbon ve kalsiyum karbonat verileri Kükrer. (2018)'den alınmıştır.

According to the elemental distribution, a normalization distribution (Mo/Al) have been used in this study in order to detect the anoxia (Kükurer, 2018). In terms of anoxia, higher values (up to 3-4) are very similar to the organic carbon concentration and carbonate ratio. In-between 60-50 cm, there is an increment of the Mo/Al ratio (up to 3). Thus, the 45-35 cm interval also has higher values (up to 3.5) (Kükurer, 2018).

According to the age-depth model (Figure 3), the studied sediment core implies that two major climatic records were perceived in the Northern Hemisphere in the last ~450 years (Kükurer, 2018). One of the climatic records is the termination of the Little Ice Age period (~30 cm) (termination at ~192 cal yrs BP). The upper part of the core is represented by the Industrial Epoch, or the most recent retreat of the glacial period (~192 cal yrs BP to the present) (Figure 4).

DISCUSSION

Termination of LIA

Based on the age-depth model, the end of LIA covers the time period from ~430 cal yrs BP to ~192 cal yrs BP (covering the 16th to 18th centuries). The end of LIA is presumably represented by increasing detrital input; however, termination of this event is generally detected by low lithogenic elemental distribution in Europe and Anatolia (Roberts et al., 2012; Kuzucuoğlu et al., 2011). The lithogenic component is produced by the surrounding volcanic rocks (Late Pliocene to Early Pleistocene basaltic lava flows; Sheth et al., 2015). Therefore, especially up to 30 cm in the study core, detrital elemental distribution has lower values compared to the rest of the core. This correlation effectively represents the accuracy of the age-depth model, as well as the ICP-MS results (Figure 4).

Similar observations have been detected on Lake Nar (Jones et al., 2006; Touchan et al., 2007) where the termination of LIA is well

represented by dry conditions. Such consistency is also documented in Lake Tecer (Kuniholm, 1990; White, 2011; Kuzucuoğlu et al., 2011). This climatic behaviour can be seen on detrital elemental proxies. Their decreasing trend indicates the drier conditions of Lake Aygır, which is surrounded by volcanic rocks. Moreover, the lake is encircled by steep mountains that cause sparse vegetation and low biological diversity (Anonymous, 2017). The fluctuations of the elemental profiles (66-30 cm) are not caused by such effects (Figure 4). Moreover, the termination of LIA has higher values of $\delta^{13}\text{C}$, which indicates lower vegetation in the vicinity. Thus, these $\delta^{13}\text{C}$ values also support the inorganic source of the organic content (Kuniholm, 1990; McDermott, 2004; Fairchild et al., 2006).

Temperature fluctuations can be traced by using $\delta^{18}\text{O}$ values. This also provides a good correlation between precipitation and evaporation. Comparing the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles, the oxygen isotope has higher values during the termination of LIA. These high values indicate drier and colder conditions (Cronin, 1999; Leng and Marshall, 2004; Jones & Roberts, 2008; Göktürk et al., 2011; Ocakoğlu et al., 2016). This is also supported by the depleted elemental distribution of the studied core (Figure 4).

Industrial Epoch

The second major period observed in the core, at a depth of 31-0 cm, is the Industrial Epoch, which was deposited between ~192 cal years BP and recent times. Because the beginning of the Industrial Revolution was around 1850, this period has been previously documented as having wet and warm characteristics. In the studied core, we observed characteristic proxies in terms of the geochemical aspects. Detrital parameters (Fe, Ti, K, Zr, Rb) exhibit an increasing trend in this period, displaying an enriched catchment area in the lake region (Figure 2 & 4). Undoubtedly, more profuse melting of the snow in the vicinity

area provided more terrestrial input into the lake. This is supported by the lower values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, suggesting an augmentation of precipitation. Moreover, the retreat of the remaining glaciers provided a more nurturing environment for human productivity, which has caused the human-induced greenhouse effect (Le Treut et al., 2007; Danladı & Akçer-Ön, 2018). Similar circumstances have been seen in Anatolian lakes, showing warmer climatic conditions (Kadioğlu et al., 1997; Ülgen et al., 2012; Tudryn et al., 2013; Danladı & Akçer-Ön 2018). During this period, the overflowing and abundant detrital input prevented the preservation of organic carbon in the lake. An extremely low carbonate ratio indicates such a condition, along with the Ca & Sr profiles (Figure 4).

CONCLUSION

Multi-proxy sedimentary records, including the TOC, carbonate percentage, elemental distribution of Zr, Rb, K, Ti, Ca, Sr and Fe, and the stable isotopes of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, were investigated in order to provide the paleoclimatic history of the last ~500 yrs of Lake Aygır on the East Anatolian Plateau. A 66 cm-long sediment core was used to evaluate the silty clay content, having a 0.16 cm/yr sedimentation rate. Detrital elemental proxies show relatively low values during the Little Ice Age; however, the Industrial Epoch was identified by the high detrital content and low $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. The LIA terminated at around ~192 cal yrs BP and the climate changed to the warmer conditions of IE. It is crucial to conduct further core recovery and geochemical analyses of Anatolian lakes in order to be more informed about the older climatic conditions that northeastern Anatolia experienced.

GENİŞLETİLMİŞ ÖZET

Göl tabanında biriken sedimanların çoklu proksi analizleri Holosen'deki iklim değişiklikleri ve buna bağlı kaya ayışma oranları ile ayışma

sonucu açığa çıkan detritik unsurların göl tabanındaki çökelme hızı hakkında çıkarımlar yapılmasını sağlar. Amaca göre göl tabanlarından alınan kısa veya uzun karotların fiziksel, kimyasal ve biyolojik proksileri yağlı veya kurak evreler hakkında önemli bilgiler vermektedir. Göle taşınan kurıntıların tane boyu dağılımları, killi, karbonatlı ve tuzlu ara birimler içerip içermemeleri, manyetik duyarlık özellikleri, pH özellikleri, organik karbon içeriği, toplam CaCO_3 içeriği, CaCO_3 polimorfları yani kalsit-aragonit dağılımı, karbonatların izotop kimyası, iz element dağılımları, fosil polenler ve diatomlar çökelme evresi boyunca değişen iklimsel ve çevresel koşulların hassas arşivlerini oluştururlar.

Bu çalışmada Kars ili Susuz ilçesinde Erzurum-Kars-Ardahan Platosu üzerinde yer alan Aygır Gölü paleoiklimsel proksiler açısından ele alınmıştır. Maksimum 30 metre derinliğe sahip bir volkanik set gölü olan Aygır Gölü 3,11 km uzunluğa, 1,86 km genişliğe ve $4,02 \text{ km}^2$ yüzölçümüne sahip olup, deniz seviyesinden 2.131 m yüksektedir. Göl çevresi ağırlıklı olarak Üst Miyosen-Pliyosen volkanitler ve Pliyosen andezitlerden oluşur. Susuz meteoroloji istasyonu verilerine göre sahada yıllık ortalama sıcaklık $4,9^\circ\text{C}$, yıllık toplam yağış ortalaması da 483 mm 'dir. Yağışların büyük kısmı, konveksiyonel hava akımlarına bağlı olarak yaz mevsiminde düşer.

Aygır Gölü'nden Kajak Sediment Karot Örnekleme kullanılarak alınan 66 cm uzunluk sıçık karotta çoklu proksi verileri ile Kuzeydoğu Anadolu'da özellikle Küçük Buzul Çağrı ve sonrasında iklimsel salınımların belirlenmesi amaçlanmıştır. 2 cm aralıklla dilimlenerek ayrılan 33 örnekte tabandan yüzeye doğru CaCO_3 , Zr, Rb, K, Ti, Ca, Fe, toplam organik karbon (TOC), $\delta^{18}\text{O}$ ve $\delta^{13}\text{C}$ izotop değerlerinin dağılışı belirlenmiş ve yaş verileri AMS radyokarbon tarihleştirmelerine göre değerlendirilmiştir.

Elde edilen veriler gölin yaklaşıklık son 500 yıllık geçmişteki paleoiklimsel tarihi ortaya

koymaktadır. Siltli kıl içeriğine sahip karotta sedimentasyon hızı 0,16 cm/yıldır. Küçük Buz Çağındaki düşük değerlerin aksine, izleyen endüstriyel dönem çökelleri yüksek kırıntı içeriği ve düşük $\delta^{18}\text{O}$ ve $\delta^{13}\text{C}$ değerleri ile temsil edilir. Yaş-derinlik modeline göre Küçük Buzul Çağı'nın sonu günümüzden yaklaşık 430 yıl ile 192 yıl öncesindeki zaman aralığına (16. ila 18. yüzyıllar) karşılık gelmektedir. Küçük Buz Çağı, günümüzden yaklaşık 192 yıl önce sona ermiş olmalıdır ve hemen ardından endüstriyel çağın daha sıcak koşulları egemen olmuştur. Nemli ve sıcak olan bu dönemde düşük $\delta^{18}\text{O}$ ve $\delta^{13}\text{C}$ değerlerine karşın Fe, Ti, K, Zr, Rb değerlerindeki artış eğilimi bu dönemdeki ısınmaya birlikte çevredeki kar örtüsünün daha hızlı bir şekilde erimesi ve yağıştaki artış nedeniyle göle daha fazla karasal girdisi ile ilgili olmalıdır.

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