JQS

Journal of Quaternary Science



Insight into summer drought in southern Italy: palaeohydrological evolution of Lake Pergusa (Sicily) in the last 6700 years

ZANCHETTA GIOVANNI,^{1,2,3,4}* D BANESCHI ILARIA,⁵ MAGNY MICHEL,⁶ SADORI LAURA,⁷ TERMINE ROSA,⁸ BINI MONICA,^{1,2,4} VANNIER BORIS,⁶ DESMET MARC,⁹ NATALI STEFANO,^{1,5,10} LUPPICHINI MARCO^{1,10} and PASQUETTI FRANCESCA¹ D

Received 18 January 2022; Revised 13 April 2022; Accepted 26 April 2022

ABSTRACT: The Sicily region (central Mediterranean) is at high risk of drying and desertification caused by current warming and land management. The aim of this study is to place current climatic changes within the past trajectories and natural climatic variability of the Holocene. For this we re-examine a sediment core retrieved at Lake Pergusa covering the last ca. 6700 years. A multiproxy investigation, and in particular the oxygen isotope composition of lacustrine carbonate ($\delta^{18}O_c$), allowed us to reconstruct decadal- to centennial-scale hydrological changes. The wettest period occurred between ca. 6700 and 6000 cal a BP. The $\delta^{18}O_c$ record indicates a new period of wetter conditions between ca. 3700 and 2400 cal a BP. In particular, a $\delta^{18}O_c$ minimum between 2850 and 2450 cal a BP overlaps with the period of the 'Great Solar Minimum' and corresponds to a dramatic reduction of arboreal pollen (AP%) and to an increase in synanthropic pollen, marking the onset of Greek colonization in the region. The longest driest interval corresponds to the Medieval Climate Anomaly, whereas the highest $\delta^{18}O_c$ values are recorded in the last 150 years. The trend of the last 3000 years suggests that, considering future climate projections, the area will experience unprecedented drying exacerbated by human impact.

© 2022 The Authors. Journal of Quaternary Science Published by John Wiley & Sons Ltd.

KEYWORDS: Central Mediterranean; Homeric minimum; Little Ice Age; Medieval Climate Anomaly; palaeohydrology; Sicily

Introduction

Since 1980, the acceleration of climatic changes in the Mediterranean region has exacerbated environmental problems, resulting from the combination of changes in land use, increasing pollution and declining biodiversity (e.g. Cramer et al., 2018). Recent model simulations for the region show that as mean global temperature increases in the 21st century, precipitation will decrease at the rate of ca. 4% K⁻¹ and temperatures will rise 20% more than the global average (Lionello and Scarascia, 2018, 2020). The reduction in precipitation will affect all seasons in the central and southern Mediterranean region with a projection of a maximum reduction in the southern sectors of 7% K⁻¹ in winter precipitation (Lionello and Scarascia, 2018, 2020). Along with human impact, reduced precipitation increases the risk of desertification in some sectors of the southern regions. Given the current negative trend in winter meteoric precipitation identified in southern Italy (e.g. Caloiero et al., 2018), Sicily is the Italian region that is most at risk of desertification, with ca.

70% of the region potentially exposed (e.g. Salvati and Bajocco, 2011). This situation represents a significant challenge for future environmental management. A correct and detailed understanding of the hydrological evolution of the region, within the more general context of long-term trajectories of the environmental and climate evolution of the Mediterranean under current warming (e.g. Giorgi, 2006, 2008; Lionello and Scarascia, 2018, 2020), needs to be accompanied by a comparison with proxy data beyond the scope of the instrumental and historical records, for the identification of potential patterns and useful analogues. Moreover, data on past conditions can also help disentangle the effects of human impact and the role it has played in exacerbating or mitigating the effects of climate changes on the environment. In particular, the oxygen isotope composition of lacustrine carbonates ($\delta^{18}O_c$) is considered a powerful proxy to reconstruct hydrological changes in the Mediterranean region (Zanchetta et al., 1999, 2012; Roberts et al., 2008, 2010; Leng et al., 2010a, 2013; Dean et al., 2015; Zielhofer et al., 2017), especially in lakes with a simple hydrological balance (Roberts et al., 2008). However, different types of lacustrine carbonates may reflect different seasons of precipitation (Leng and Marshall, 2004). Considering the

*Correspondence: Z. Giovanni, as above. E-mail: giovanni.zanchetta@unipi.it

¹Dipartimento di Scienze della Terra, University of Pisa, Pisa, Italy

²Centre for Climatic Change Impact (CIRSEC), University of Pisa, Pisa, Italy

³Istituto di Geologia Ambientale e Geoingegneria, CNR, Roma, Italy

⁴Istituto Nazionale di Geofisica e Vulcanologia, Rome, Italy

⁵Istituto di Geoscienze e Georisorse IGG-CNR, Via Moruzzi 1, Pisa, Italy

⁶CNRS-UMR6249, Laboratoire Chrono-Environnement, UFR des Sciences et Techniques, Besançon, France

⁷Dipartimento di Biologia Ambientale, Università di Roma "La Sapienza", Roma, Italy

⁸Laboratory of Sanitary Environmental Engineering - Section of Biology, "Kore" University of Enna, Enna, Italy

⁹Département Géosciences-Environnement, Universitè F. Rabelais de Tours, Faculte des Sciences et Techniques, Tours, France

¹⁰Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Florence, Italy

prevailing influence of oxygen isotopic composition of lake water ($\delta^{18}O_w$) on $\delta^{18}O_c$ values in the Mediterranean, $\delta^{18}O_c$ can indicate the combined effect of lake water recharge season, the period of carbonate precipitation (Zielhofer *et al.*, 2017) and the effect of evaporation (Roberts *et al.*, 2008; Leng *et al.*, 2010a, 2013). Authigenic (bio-induced) carbonates mostly precipitate during the warmer part of the year (late spring to summer, e.g. Leng and Marshall, 2004; Lacey *et al.*, 2016) and their $\delta^{18}O_c$ values should record prevailing summer conditions (Leng and Marshall, 2004; Bini *et al.*, 2019). Therefore, $\delta^{18}O_c$ in lacustrine records can contribute to reconstructing changes in the recharge seasons and the long-to short-term periods of drought in summer (Bini *et al.*, 2019; Roberts *et al.*, 2008; Zielhofer *et al.*, 2017).

Lake Pergusa, (central Sicily, southern Italy, Fig. 1A) is a particularly important protected area to study palaeoenvironmental and palaeoclimate evolution. It is also a strategic site to interpret the history of vegetation and human impact at the scale of the central Mediterranean basin, as demonstrated by several multiproxy studies (Sadori and Narcisi, 2001; Zanchetta et al., 2007; Roberts et al., 2008; Sadori et al., 2008, 2013, 2016). In this work, we return to this site to re-examine the lacustrine sedimentary succession and provide a new high-resolution multiproxy geochemical study of the previously investigated core PG2 (Fig. 1A; Sadori et al., 2013). The last ca. 2000 cal a BP of the isotopic record was presented in Sadori et al. (2016), but the full sequence provides an important and more complete insight into the palaeolimnological and palaeoclimatic evolution of the site over the last ca. 6700 cal a BP. The information obtained from the site will support investigation of future trends and trajectories of local environmental changes.

Site description

Study area

Lake Pergusa is located in the centre of Sicily (37°30′50"N, 14°18'21"E, Fig. 1A), at 667 m a.s.l. and it occupies a subelliptical basin with a catchment area of ca. 7.5 km², which mostly comprises Middle to Late Pliocene calcarenitic and silty-clay marine deposits (Battaglia et al., 1991). The lake has an endorheic character with no significant inlets and outlets, so that the hydrological budget is mainly controlled by rainfall, evapotranspiration, and local groundwater flow (Battaglia et al., 1991; Grasso et al., 2003; Pallalardo et al., 2006). Lake Pergusa is cited in Ovid's Metamorphoses, since it is linked to the Greek myth of Demeter-Persephone. Alongside its historical and natural interest, since the 1960s the lake has been subject to intense human pressure due to the progressive expansion of the city of Enna. The lake has also witnessed important well-water extraction and the construction of a racetrack around the perimeter of the lake, resulting in the size and depth of the lake being dramatically reduced, and leading to a substantial increase in water salinity (Battaglia et al., 1991; Grasso et al., 2003; Pappalardo et al., 2006). As a result of the natural and ecological value of the lake, in the last few decades specific policies of environmental protection have been promoted by the Regional Province of Enna (today 'Libero Consorzio Comunale di Enna'), including the recognition of Pergusa as a Site of Communitarian Importance under the European 'Habitat' Directive (Termine, 2006), and the introduction of external water between 2002 and 2003 (Amore and Termine, 2005).

The endorheic character of the lake makes it very sensitive to seasonal and short-term alterations in rainfall, which produce many changes in terms of lake size and depth, as reported since the end of the 19th century (Sadori and Narcisi, 2001, and references therein).

Climate, hydrogeochemistry and stable isotope geochemistry

Precipitation was above the average for the period 1940–1960, as indicated by the cumulative monthly rainfall (CMR) values and by cumulative annual rainfall (CAR) (Fig. 1B). After this period, there was a progressive decrease in precipitation. A sporadic increase in rainfall occurred between 1995 and 2010. Mean CAR is about 750 mm. In those years, the area was characterized by maximum values of rainfall in November, December and January, with an average of about 100 mm for each month. Minimum values are recorded in the summer months of June, July and August with an average rainfall of about 20 mm in June and August, and 10 mm in July. The spring months are characterized by a progressive decrease in rainfall from March to May.

Over the last century, maximum values of temperature have been recorded in summer with mean temperatures of about 23 °C and minimum values in January and February, with mean temperatures of about 5 °C. We observed an increase in temperature from 1930 to 2010, as shown by the annual anomalies based on the 1951–1980 period (black line in Fig. 1D). The mean increase rate was 0.01 °C a⁻¹. In more detail, the time series is characterized by periods with lower temperatures (such as 1955–1965 and 1980–1985) and periods with higher temperatures (such as 1935–1940, 1990–2000).

Chemical data from Lake Pergusa have been summarized by Battaglia et al. (1991). However, in 2005-2006 the Regional Province of Enna promoted environmental monitoring led by the Sicilia Ambiente S.p.A. The lake water temperature ranged from about 4 to 26 °C (Amore and Termine, 2005, 2007). The results revealed that the temperature of waters at different depths was the same throughout the year, except for late spring or early autumn when the surface waters were warmer than at the bottom of the lake. In a vertical profile the pH changed from 7.28 to 8.86, with an average value of 7.92. The electrical conductivity measured in the period 2005-2006 showed an average value of 8.83 mS cm⁻¹, not far from the average of 14.5 mS cm⁻¹ recorded in 2003–2004, but much lower than the average of 87.5 mS cm⁻¹ recorded during 2001–2002 monitoring. The conductivity measured in bottom water presented an average of 8.8 mS cm⁻¹, similar to that of the surface waters. Dissolved oxygen saturation measured at the surface was 77.5% on average, with a minimum value of 19.4% in August 2006 and a maximum of 158.1% in April 2006. At the bottom, dissolved oxygen saturation is much lower, with an average of 44.8%. Further monitoring was performed for this study (see the Methods and Results sections). The lake water belongs to the sulphatechloride-alkaline facies, while the groundwaters are sulphate-chloride-earth alkaline, denoting that the lake is also fed by the aquifer. In particular, chloride, sodium and sulphate contents are higher in lake water than in groundwater, owing to the evaporation of lake water (Amore and Termine, 2007). Indeed, the maximum monthly evaporation in the period 2002-2006 ranged from 1 to 61 mm, with the highest values recorded in summer.

The monthly isotopic composition of precipitation in Sicily shows a large variability (Liotta *et al.*, 2013) typical of precipitation over the Mediterranean area, reflecting seasonal changes controlled by meteorological variables (e.g. moisture sources, air temperature, rainfall amount) as well as the

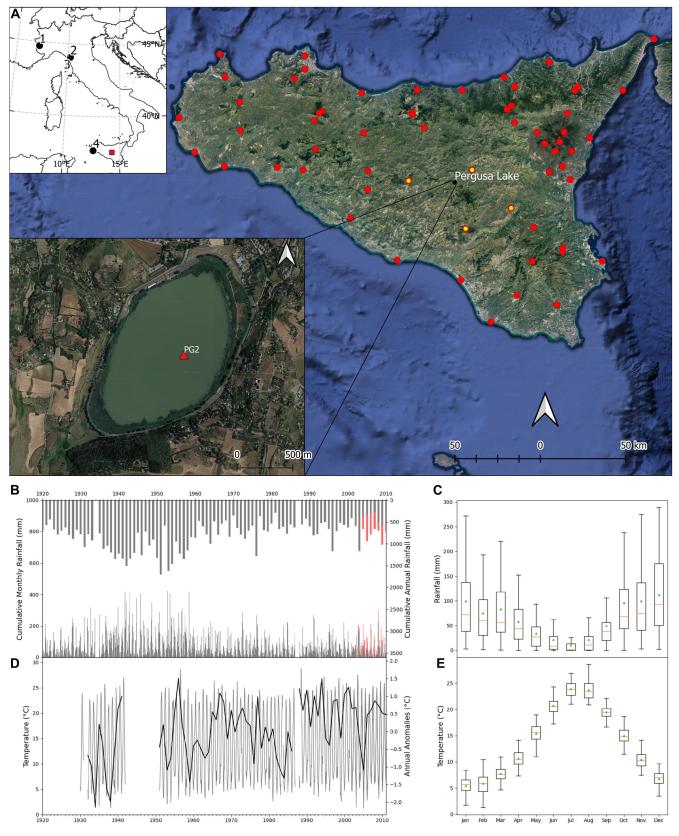


Figure 1. (A) Location map of Lake Pergusa. (B) Cumulative monthly (and annual) rainfall. (C) Rainfall boxplots. (D) Monthly temperature over time and annual anomalies (anomalies calculated using 1951–1980 as the reference period). (E) Temperature boxplots. Rainfall data were provided by Osservatorio delle Acque (Sicily Region, http://www.osservatorioacque.it/) for the period 1920–2003, Lago di Pergusa (Libero Consorzio Comunale di Enna, http://riserveenna.it/; red bars) for the period 2002–2010, and World Meteorological Organization (WMO) and National Oceanic and Atmospheric Administration (NOAA, https://www.ncdc.noaa.gov/cdo-web/search) for the period 2001–2010. Temperature data were provided by Osservatorio delle Acque (Sicily Region, http://www.osservatorioacque.it/) for the period 1929–2010 and WMO and NOAA for the period 2001–2010. In the boxplots: the orange line represents the median, the green triangle the mean. The box represents the interval between the 25th and 75th percentiles. Where IQR is the interquartile range (Q3–Q1), the upper whisker will extend to the last datum (less than Q3 + 1.5*IQR). Similarly, the lower whisker will extend to the first datum greater than Q1 – 1.5*IQR. 1: Rio Martino cave; 2–3 Renella and Corchia Caves; 4 Lake Preola. [Color figure can be viewed at wileyonlinelibrary.com]

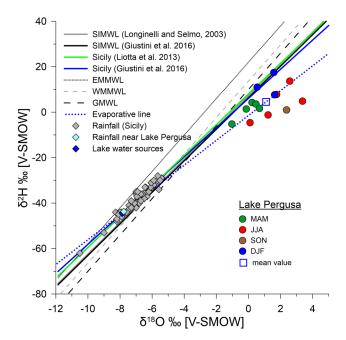


Figure 2. δ²H vs. δ¹⁸O plot of Lake Pergusa water samples along with the annual weighted mean isotopic values of precipitation in Sicily (Giustini *et al.*, 2016; Liotta *et al.*, 2013). The mean isotopic composition of precipitation computed from the data recorded at the four sites closest to Lake Pergusa is also shown (light blue square). The blue square represents the intersection between the evaporative line (EL) defined by the lake water samples (blue dotted line) and local meteoric water line (LMWL) in Sicily. The lake water samples are grouped by season. Also shown: Eastern Mediterranean Meteoric Water Line (EMMWL, Gat and Carmi, 1970); Western Mediterranean Meteoric Water Line (WMMWL, Celle-Jeanton 2000); Global Meteoric Water Line (GMWL, Craig, 1961, Rozanski *et al.*, 1993). [Color figure can be viewed at wileyonlinelibrary.com]

influence of geographical factors (e.g. altitude, distance from the coast). Figure 2 shows the annual weighted mean isotopic values of precipitation in Sicily from different stations, collected by Giustini *et al.* (2016) and previously published by other authors (e.g. Liotta *et al.*, 2006, 2013). The data define a local meteoric water line (LMWL, blue line in Fig. 2), with a slope of 6.42 (Giustini *et al.*, 2016). According to Liotta *et al.* (2013), the mean δ^{18} O in this area should range between ca. –6.5 and –7.5‰.

Materials and Methods

Core PG2 is a 6.26-m-long sediment core retrieved in Lake Pergusa (Fig. 1A) in 2006 during a study within the project LAMA (Magny *et al.*, 2013) by using a UWITEC coring platform with percussion piston coring. The core is mostly composed of the relatively homogeneous carbonate lake-marl. The age model for PG2 was presented in detail by Sadori *et al.* (2013). It is based on four radiocarbon dates obtained from terrestrial plant macrofossil remains and one tephra layer of known age (Fig. 3). The age model was calculated using the program Clam (Blaauw, 2010), which calibrated the ¹⁴C dates following IntCal09 (Reimer *et al.*, 2009). The new calibration curve (Stuiver *et al.*, 2021) introduces no significant differences (within the age model error), and for this reason the model has not been modified.

Samples were collected every 6 cm from the core, dried in an oven at $50\,^{\circ}$ C for 48 h, and prepared at the Laboratory of Paleoclimatology and Geoarchaeology of the University of Pisa and at the IGG-CNR of Pisa. Samples for stable isotopes on the bulk fraction were gently disaggregated and sieved at $100\,\mu m$ to separate biogenic remains (e.g. ostracods and shells) from the

sediments; the fraction below 100 µm was powdered and homogenized. Carbonate isotopic compositions were determined on CO₂ released by an overnight reaction with 100% H₃PO₄ at 25 °C and purified using cryogenic traps at the Stable Isotope Laboratory of the IGG-CNR in Pisa. Mass spectrometric measurements were normalized to the Vienna Pee Dee Belemnite scale using an internal working standard (Carrara Marble), calibrated against the international standards NBS18 and NBS19. Due to the high ratio between carbonate content and organic matter (total inorganic carbon/total organic carbon, i.e. TIC/TOC: 0.96 ± 0.61), no pretreatment was performed to remove sedimentary organic matter, following the general results of Wierzbowski (2007), Oehlerich et al. (2013) and Mannella et al. (2020). The isotopic ratios are reported in the well-known δ-notation ‰ (per mill). The average analytical precision $(\pm 1\sigma)$ for replicate analyses of carbonate was ≤0.15% for both carbon and oxygen. Herein, the oxygen and carbon isotopic composition of these samples (known as 'bulk') are represented by the notation $\delta^{18}O_c$ and $\delta^{13}C_c$, respectively.

An aliquot of each sample was treated with 10% HCl to remove carbonates for 48 h, then washed several times with deionized water to neutral pH, and dried again at 40 °C. The carbon isotope composition of bulk organic matter was obtained at the IGG-CNR of Pisa by producing CO2 from combustion using a Carlo Erba 1108 elemental analyser, interfaced to a Finnigan Delta Plus Advantage via the Finnigan MAT Conflo II interface, and calibrated using international standards IAEA-CH6 (δ^{13} C = -10.45‰) and IAEA-CH7 (δ^{13} C = -32.15%); graphite within-run standard was measured to check the performance and possible drift deviations of the instrument. Mean analytical reproducibility of these samples was ≤0.1‰. In this paper we refer to the isotopic composition of these samples with the notation $\delta^{13}C_{om}$. Compared to the other proxies, $\delta^{13}C_{om}$ was analysed at lower resolution (ca. 12 cm on average).

The concentrations of total carbon (TC) and of total nitrogen (TN) were measured with a Carlo Erba 1108 elemental analyser, and the measurements were calibrated against an Acetanilide standard (precision generally <0.3%). TIC was determined by gasometry (with calibration to pure calcite), as described by Leone *et al.* (1988). Mean analytical precision is usually <5%. TOC was obtained from the difference between TC and TIC, and CaCO₃ content (%) was obtained assuming that all TIC derived from carbonate minerals.

The lake water was monitored monthly for stable isotopes and chloride ions from April 2010 to July 2011. The oxygen isotope composition of lake water was determined by the water— CO_2 equilibration method at 25 °C (Epstein and Mayeda, 1953) by using a Finnigan MAT 252 isotope ratio mass spectrometer (IRMS) at IGG-CNR in Pisa. For hydrogen isotope analysis, waters were reduced to H_2 using zinc and following the method of Coleman *et al.* (1982), and were analysed using a Europa Scientific GEO 20-20 IRMS. The water isotope data are reported with respect to V-SMOW and are indicated as $\delta^{18}O_{lake}$.

Several samples of catchment rocks were collected in the field to compare their isotope composition with those of lacustrine sediments in order to detect possible contamination of the authigenic lacustrine carbonate fraction (Zanchetta *et al.*, 2007). All the proxy data from core PG2 are reported as Supplementary Material in Table S1.

Results

All water samples from the lake have higher isotope values compared to the annual mean from Sicily and most samples

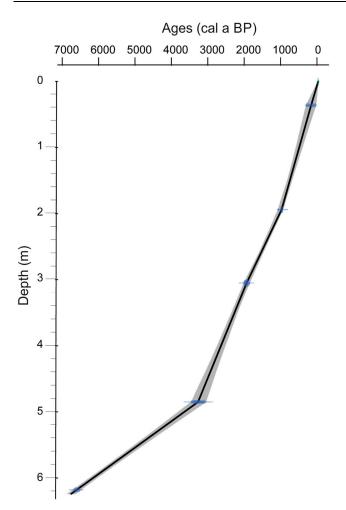


Figure 3. PG2 core age model (after Sadori *et al.*, 2013). The age model was calculated using the program Clam (Blaauw, 2010), which calibrated the ¹⁴C dates following IntCal09 (Reimer *et al.*, 2009). [Color figure can be viewed at wileyonlinelibrary.com]

departed from the LMWL and defined an evaporation line (EL) with a lower slope compared to that of the LMWL (Fig. 2). EL was computed by using reduced major axis (RMA) regression, which proved to be more suitable to fit the isotope data of natural water (Crawford et al., 2014; Marchina et al., 2020). The EL slope is commonly used to correct the evaporation effects on the collected samples by identifying the EL-LMWL intersection point, which provides the theoretical isotope composition of the source water prior to evaporation (Gat, 1996; Bowen et al., 2018). The regression approach using multiple samples is the most common method employed to estimate EL. This approach assumes that water in open basins has a fixed initial isotopic composition and only changes in response to variations in the degree of evaporation. This assumption is seldom true in natural basins and it can produce systematic biases in EL slope and source water isotope composition estimates. However, the reliability of EL can be proven by comparing the theoretical isotopic value of source water with values for one or more hypothesized source (Bowen et al., 2018). As shown in Fig. 2, the intersection between EL and LMWL in Sicily yields a theoretical isotopic value of source water of -7.9% for $\delta^{18}O$ and = -44.5% for δ²H. This value is very similar to the annual weighted mean isotopic composition of precipitation recorded at the four sites closest to Lake Pergusa (yellow dots in Fig. 1A; = -7.77 and =-43.7% for δ^{18} O and δ^{2} H, respectively), thus confirming the reliability of EL and confirming that lake water is mostly

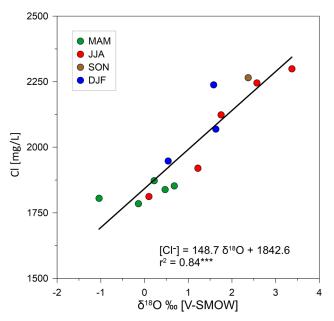


Figure 4. Relationship between Cl⁻ in Lake Pergusa water and δ^{18} O values. Different colours indicate samples of different seasons. Green: spring; red: summer; brown: autumn; blue: winter. ***p < 0.001. [Color figure can be viewed at wileyonlinelibrary.com]

recharged from local rainfall and very local groundwaters (Pappalardo *et al.*, 2006).

Both $\delta^{18}O_{lake}$ and Cl^- show a strong linear relationship, indicating that lake salinity is strongly related to local evaporation and that $\delta^{18}O_{lake}$ is also a good proxy for lake salinity (Fig. 4).

The age model indicates that the record represents the last ca. 6700 years (Fig. 3; Sadori *et al.*, 2013) with a sample resolution ranging from ca. 30 to 130 a (average 64 ± 35 a), with higher resolution (<50 a) in the first ca. 3000 years. The sedimentation rate is ca. 0.05 cm a⁻¹ from 6700 to 3200 years, which increases to ca. 0.13 cm a⁻¹ in the younger section. This produces a higher sampling resolution in the last 3200 years compared to the lower section of the core.

Figure 5 shows the lacustrine proxies obtained from the PG2 sediment.

- The carbonate (CaCO₃%) content ranges from ca. 5 to 60% (average 41.6±11%). After a first short phase of lower values, CaCO₃ content rapidly increases at ca. 6000 cal a BP, showing a constant increase until 3000 cal a BP. The values rapidly decrease, showing an interval of relatively low values between ca. 3000 and 2400 cal a BP, then they rise again, oscillating at around 40% in the last ca. 2000 years.
- C/N atomic ratio is on average 13.3 ± 2.5 ranging from ca. 4 to 18, and indicating mixed lacustrine (probably dominant) and terrestrial sources of organic matter; indeed, algae typically have atomic C/N ratios between 4 and 10, whereas vascular land plants have C/N ratios of >20 (e.g. Meyers, 1994, 2003). No particular trends (with the exception of some local spikes) are discernible in the record.
- − The $δ^{13}C_{om}$ has an average value of −22.9 ± 2‰ and a range of ca. 8‰ (from ca. −17 to −25‰) where C/N vs. $δ^{13}C_{om}$ (Fig. 6) supports the notion of sedimentary organic matter of mixed origin (e.g. Meyers, 2003). However, similar to the C/N record, $δ^{13}C_{om}$ shows no evident trends.
- The mean TOC value is 6.4 ± 3% with a range of ca. 18% (from ca. 1 to 19%). TOC values are appreciably higher before ca. 2800 cal a BP (average values 8.8%), with the highest values until 5700 cal a BP, followed by a sharp drop

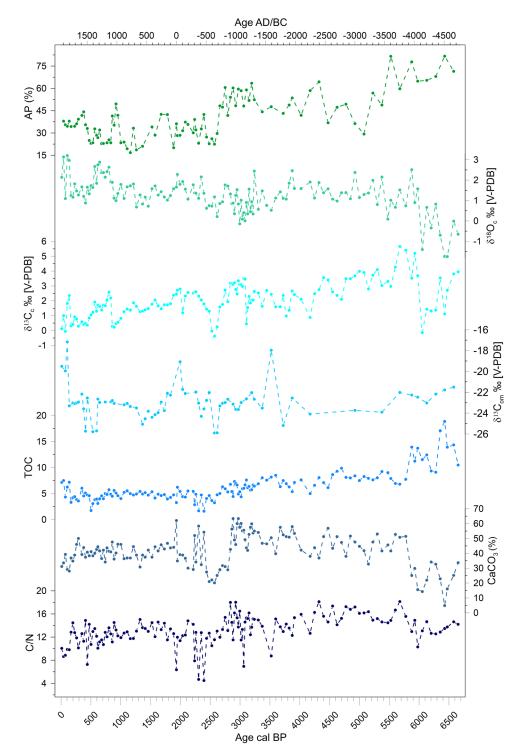


Figure 5. Proxy data from the Pergusa record obtained from the PG2 core. Arboreal pollen (AP) percentage after Sadori *et al.* (2013). As in the text, $\delta^{18}O_c$ and $\delta^{13}C_c$ indicate the isotopic composition of bulk carbonate fraction, and $\delta^{13}C_{om}$ is referred to the isotopic composition of total organic carbon (TOC). [Color figure can be viewed at wileyonlinelibrary.com]

and gradual decrease until ca. 2800 cal a BP, when the values tend to remain constant at ca. 5%.

- The $\delta^{13}C_c$ record has a mean value of +2.1 ± 1.0% with a range of ca. 5% (from ca. *vs* 0.4 to +5.2%). The record shows a progressive decrease in isotopic values, with several evident oscillations for example at 6300–6000, 2700–2550, 1000–900 and 400–0 cal a BP all characterized by lower $\delta^{13}C_c$ values.
- The $\delta^{18}O_c$ record shows mean values of +1.3 \pm 1.0%, with a range of ca. 5% (from ca. +3.2 to vs 1.7%). The lowest $\delta^{18}O_c$ values are present in the first 200 years of the

succession, and then increase rapidly at ca. 6000 cal a BP, with relatively higher values in the interval between 6000 and 3900 cal a BP. The relatively lower resolution of this interval makes it impossible to describe the decadal- to centennial-scale shorter oscillations in further detail. A possible short interval of lower values is present at ca. 5400 cal a BP. Starting from 3500 cal a BP, the resolution allows the definition of intervals of higher/lower values in more detail. Clear intervals with lower $\delta^{18}{\rm O}_{\rm c}$ are found at ca. 3200–2900 cal a BP. In particular, intervals of higher $\delta^{18}{\rm O}_{\rm c}$ are present at 3100–2900, 1450–1250 and 500–200

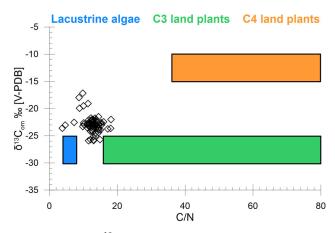


Figure 6. C/N vs. $\delta^{13}C_{om}$. Composition for lacustrine algae, C3 and C4 plants after Meyer (2003). The field for $\delta^{13}C$ of the algae depends on the initial composition of dissolved inorganic carbon (DIC). [Color figure can be viewed at wileyonlinelibrary.com]

Table 1. Spearman correlation coefficients between different proxies of core PG2. Significant correlations are in bold (p < 0.05 = 95%).

	$CaCO_3$	$\delta^{13}C_{\rm c}$	$\delta^{18}O_c$	$\delta^{13}C_{om}$	TOC%	C/N	AP%
CaCO ₃	_						
$\delta^{13}C_c$	0.32	_					
$\delta^{18}O_c$	-0.04	-0.09	_				
$\delta^{13}C_{om}$	-0.08	0.13	0.05	-			
TOC%	-0.10	0.49	-0.27	0.20	-		
C/N	0.13	0.44	-0.25	-0.26	0.57	_	
AP%	0.18	0.36	-0.22	0.27	0.57	0.34	-

cal a BP, showing a more complex interval with higher values in between. The highest $\delta^{18}O_c$ values are observed in the last 130 years of the record and an additional interval of higher values is seen between ca. 550 and 850 cal a BP.

Discussion

Palaeolimnological proxies

In line with the mixed nature of the organic matter of the lake as indicated by the $C/N-\delta^{13}C_{om}$ relationship (Fig. 6)—there is no apparent correlation between $\delta^{13}C_c$ and $\delta^{13}C_{om}$ (Table 1): indeed, if organic matter and carbonate originate from the same pool of lacustrine dissolved inorganic carbon (DIC), the $\delta^{13}C_c$ and $\delta^{13}C_{om}$ values should show a high degree of correlation (e.g. Zanchetta et al., 2018). There is no statistically significant correlation between $\delta^{13}C_c$ and $\delta^{18}O_c$ (Table 1). It has been suggested that a strong correlation between $\delta^{13}C_c$ and δ¹⁸O_c indicates closed lake (endorheic) conditions (Talbot, 1990), which does not seem to be a generalized application, at least considering the Pergusa isotopic data. However, the presence of clastic carbonate material can corrupt the isotopic signal (Leng et al., 2010b; Zanchetta et al., 2012) and its potential presence can be suggested by the input of terrestrial organic matter. Zanchetta et al. (2007) have already discussed the negligible influence of the clastic component in the isotopic record of Pergusa sediments, but cores retrieved in different sectors of the lake can show different contaminations. Figure 7 shows the isotope composition of the calcarenitic layers of the Pliocene marine succession collected in the Pergusa catchment, compared with the values of the lacustrine sediments. The calcarenitic

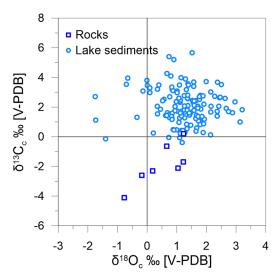


Figure 7. $\delta^{13}C_c$ vs. $\delta^{18}O_c$ of lacustrine carbonates and catchment rocks. Catchment rocks and lacustrine carbonates generally have no overlapping values. [Color figure can be viewed at wileyonlinelibrary.com]

layers show a large compositional range but their isotopic values overlap only marginally with those of the lacustrine carbonates, indicating that they have little influence on the final isotope composition of the lacustrine carbonate deposits. Indeed, in contrast to generally higher $\delta^{13}C_{\rm c}$ and $\delta^{18}O_{\rm c}$ values of the lacustrine carbonate, the marine calcarenitic samples have much lower isotopic values. In particular, the lowest $\delta^{13}C_{\rm c}$ and $\delta^{18}O_{\rm c}$ values of the calcarenitic layers indicate the presence of diagenetic cements of meteoric origin (e.g. Lohmann, 1988).

With no significant clastic carbonate contamination, CaCO₃ content can be considered a proxy for primary productivity related to dissolved CO₂ consumption by algae during photosynthesis. This may induce carbonate precipitation (e.g. Leng and Marshall, 2004; Francke et al., 2016) and preservation if no subsequent carbonate dissolution occurs. Similarly, TOC content can indicate the extent of primary productivity even though organic matter can be susceptible to different degrees of recycling, for instance due to the biological activity in the water column and bottom redox conditions (Meyers and Ishiwatari, 1993; Meyers, 2003). This activity can be regulated by different factors including lake-level changes. Although CaCO₃ and TOC do not show a significant correlation (Table 1), which may depend on the fact that TOC is partially contaminated by clastic terrestrial organic matter, they do present a very similar pattern of changes. The CaCO₃ and TOC records suggest that the last 3000 years have been characterized by lower lake primary productivity compared to the period between ca. 5800 and 3000 cal a BP (Fig. 5). However, in the first part of the record (from ca. 6500 to 5800 cal a BP) CaCO3 and TOC are in antiphase, with increasing TOC and decreasing CaCO₃ content. This relationship may indicate an increase in organic matter preservation accompanied by a reduction in carbonate precipitation or by partial dissolution after precipitation. This might be related to a higher lake level producing a minor degree of oxygenation at the lake bottom increasing organic matter preservation, and to minor 'saline' water, less prone to precipitate carbonate.

Despite several important differences, in some intervals the CaCO $_3$ – and then the TOC– record resembles the $\delta^{13}C_c$ record (Fig. 5), which typically reflect the carbon isotope composition of the DIC ($\delta^{13}C_{DIC}$, Leng and Marshall, 2004). In turn, the $\delta^{13}C_{DIC}$ is influenced by several processes such as equilibration with atmospheric CO $_2$, photosynthetic activity

within the lake, outgassing, recycling of organic matter (including methanogenesis) and isotopic composition of inflowing CO2 (e.g. Hollander and McKenzie, 1991; Leng and Marshall, 2004; Gu et al., 2004; Zanchetta et al., 2018). High $\delta^{13}C_{c}$, like most of the values in the Pergusa record (>0%), is promoted by high equilibration with atmospheric CO₂, strong evaporation (which favours outgassing of isotopically light ¹²CO₂), and high removal rate of ¹²CO₂ by photosynthetic activity, low recycling and high organic matter burial (e.g. Talbot, 1990; Meyers, 2003; Zanchetta et al., 2007). For instance, Gu et al. (2004) found anomalously high $\delta^{13}C_{DIC}$ in the shallow Lake Apopka by combining effects of low terrestrial CO2 inflow, high sedimentation, intensive methanogenesis followed by ebullition, and high primary activity. Therefore, the generally higher TOC and CaCO₃ content between ca. 3000 and 5000 cal a BP roughly matches higher δ¹³C_c values, consistent with higher productivity, higher burial and/or lower recycling of organic matter. In contrast, lower $\delta^{13}C_c$ values during the late part of the Holocene are consistent with lower CaCO₃ content and lower TOC accumulation. A particularly evident phase of lower δ¹³C_c values associated with a decrease in CaCO₃ is centred at ca. 2600 cal a BP, with also a less evident decrease in TOC. A more complex situation is present in the first part of the record where-along with the highest TOC values—there are lower CaCO3 but variable $\delta^{13}C_{\rm c}$ values, with an interval of lower values between ca. 6300 and 6000 cal a BP (Fig. 5). This combination of values in the lower part of the record can indicate a higher lake level and higher freshwater input from the catchment. Higher freshwater input from the catchment can imply greater leaching of low δ¹³C_c soil CO₂, compensating for the effect of increasing preservation of the organic matter within the lake (Whittington et al., 2015; Zanchetta et al., 2018). This interval is generally characterized by higher arboreal pollen percentage (AP%, Sadori et al., 2013; Fig. 5), indicating greater treecover in the catchment, which suggests enhanced soil development and landscape stability in a warmer and wetter climate (Sadori and Narcisi, 2001; Sadori et al., 2013) supporting the proposed interpretation.

The AP% curve shows a tripartition of the Holocene (as for the CaCO₃ and TOC records, even if not perfectly coincident from a chronological point of view), which may suggest that vegetation cover influencing soil activity, in the sense of weathering and hydrology (e.g. Kelly et al., 1998), controls the delivery of nutrient and dissolved ions to the lacustrine system at the millennial scale. In recent millennia, part of the change in the arboreal cover in this area has been driven by anthropogenic forest clearance and land-use changes (Sadori and Narcisi, 2001; Sadori et al., 2013, 2016), and this may have had an indirect effect on the lake chemistry regulated by weathering processes (e.g. Bayon et al., 2012) and nutrient delivery. According to this interpretation, we would expect the progressive reduction in the AP% to have produced a decrease in soil CO₂ production and a reduction of the flush of leached soil CO_2 (reducing the supply of low $\delta^{13}C_c$ carbon to the lake; e.g. Cerling and Quade, 1993; Meyers, 2003; Zanchetta et al., 2018). This should have progressively promoted an increase in $\delta^{13}C_{\rm c}$ values, inconsistent with the observed longterm trend of $\delta^{13}C_{\rm c}$ (Fig. 5). However, a progressive long-term increase in organic matter recycling, for instance, might have generated the general decreasing trend evident in $\delta^{13}C_c$ values, compensating for the reduction of soil CO₂ supply.

Palaeohydrological reconstruction

 $\delta^{18}O_c$ mostly depends on water temperature, $\delta^{18}O_w$ of lake water and eventual kinetic isotopic effects, which may result

from the rate of mineral precipitation (Teranes et al., 1999; Ito, 2001). However, in most of the Mediterranean region, the dominant factor driving $\delta^{18}O_c$ is believed to be the change in $\delta^{18}O_w$ controlled by the hydrological balance of the lake (e.g. Zanchetta et al., 1999, 2007; Roberts et al., 2008). This may be accompanied by changes in the isotopic composition of rainfall related to the 'amount effect' (Bard et al., 2002; Zanchetta et al., 2007) and/or to different origins of precipitation (e.g. Bard et al., 2002; Celle-Jeanton et al., 2001). Interestingly, Natali et al. (2021) reported a significant and very strong negative correlation (r = -0.90) between monthly mean rainfall amount and δ^{18} O of monthly collected rainfall (-4.4% per 100 mm month⁻¹) in the period 1976-1978 and 2004 at the Palermo rainfall station, one of the longest isotopic time series in precipitation of southern Italy (IAEA/WMO, 2020). The correlation was slightly lower (r = -0.63) when raw monthly data were used (-2.5% per 100 mm month⁻¹). Therefore, it is reasonable to assume that a decrease in precipitation produces a general increase in the $\delta^{18}O$ of recharge water. The $\delta^{18}O_w$ of Lake Pergusa is strongly affected by summer-autumn evaporation (Fig. 2), which corresponds to the period of bio-induced carbonate precipitation, and therefore $\delta^{18}O_c$ seems to reflect the effects of summer conditions, even if repeated evaporation and winter recharge (specifically the 'amount effect', Bard et al., 2002) can modulate the signal on a longer temporal scale. However, the absence of an important inlet from a large catchment is likely to attenuate the importance of the isotopic signal of the yearly recharge season. Therefore, a higher $\delta^{18}O_c$ can be considered as the result of a succession of particularly drier summers probably coupled with lower winter recharge, whereas lower values might indicate generally wetter conditions.

To better highlight the long-term trend and the centennial-scale fluctuation, the $\delta^{18}O_c$ record was transformed into z-scores (Fig. 8); that is, the record mean was subtracted from each proxy value, and the difference was divided by the record's standard deviation.

Considering the intervals where the z-score exceeds $\pm 1\sigma$ of the mean and excluding single values, the first ca. 500 years of the record (until ca. 6000 cal a BP) represent the wettest period and probably the wettest summers and this is in agreement with previously published low-resolution data reported by Zanchetta et al. (2007) and Roberts et al. (2008). These data indicate that the Early and part of the Middle Holocene were characterized by lower δ¹⁸O_c values, indicating wetter conditions, as also reported in other areas of the Mediterranean (e.g. Roberts et al., 2008). This scenario is consistent with the higher lake level for this period inferred from other proxies and it corresponds to the period of higher AP%, as discussed in the previous section. Higher lake levels during the Early to Middle Holocene are also reported for Lake Preola in western Sicily (Magny et al., 2011; Fig. 8). Even if the $\delta^{18}O_c$ may follow centennial-scale lake-level oscillations in simple hydrological systems (e.g. Baneschi et al., 2020), the $\delta^{18}O_c$ evolution of Lake Pergusa does not follow the Preola lake level trends (Fig. 8), indicating that the response of $\delta^{18} O_c$ and lake level changes are unique to individual lake systems and cannot be exported at a regional level.

The interval between ca. 6000 and 3700 cal a BP is generally drier compared to the beginning of the record, but with some shorter oscillations. The low resolution of this interval prevents good definition of a single interval but, with the exception of some single values, no intervals significantly exceed $\pm 1\sigma$ of the average value. There is an interval of higher $\delta^{18}O_c$ between ca. 4500 and 3800 cal a BP, although it is not very prominent. This interval may possibly represent the hydrological complexity connected to the '4.2 event' (Weiss, 2016) that seems to exist

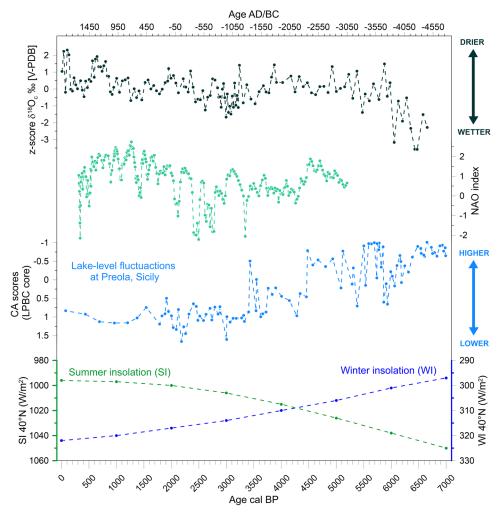


Figure 8. From top to bottom: comparison between z-score of $\delta^{18}O_c$ (this work); proxy for NAO index (Olsen *et al.*, 2012); lake level at Lake Preola (Magny *et al.*, 2011); and summer and winter insolation at 40°N (Berger and Loutre,1991). [Color figure can be viewed at wileyonlinelibrary.com]

in the Mediterranean (e.g. Magny et al., 2009; Zanchetta et al., 2012, 2016; Isola et al., 2019; Bini et al., 2019). However, this is not a very prominent drier interval, which may suggest that in the Pergusa record the '4.2 event' is not marked by a prominent period of dry summers. This would support the hypothesis, put forward by Bini et al. (2019), of possible cooler and wetter summers during this interval in a part of the Mediterranean, perhaps associated with drier winters. Wetter conditions were generally present between 3700 and 2900 cal a BP (1750-950 BC), with the most prominent interval from ca. 3200 to 2900 cal a BP (1250-950 BC). At ca. 2800 cal a BP (850 BC) there is a short period of drier conditions, followed of a new phase of wetter conditions between 2850 and 2450 cal a BP (ca. 900-500 BC), even if still below $\pm 1\sigma$. The interval between 2400 and 1500 cal a BP (ca. 350 BC to 500 AD) shows alternating but generally drier conditions compared to the previous intervals, despite a relatively wetter interval centred at 1700 cal a BP (ca. 250 AD). However, all these changes are within the $\pm 1\sigma$ of the longterm average. A wetter interval is recorded between 1450 and 1250 cal a BP (ca. 500-700 AD). Drier conditions seem to return after ca. 1250 cal a BP (700 AD), with a wetter spike at ca. 900 cal a BP (ca. 1050 AD). However, the most prominent and longest dry interval-at least of the last 3000 years-is present from ca. 850 to 550 cal a BP (ca. 1050-1550 AD). This event is followed by a ca. 300-year wetter interval (from ca. 550 to 180 cal a BP-1800-1550 AD). Despite some oscillations, from 180 cal a BP, the $\delta^{18}O_c$ values (ca. 1800 AD) increase again and are

the highest of the record, suggesting a phase of unusually high evaporation of the lake waters for the last 3000 years (Figs. 8 and 9).

Insight into the last three millennia: human impact and relationship with North Atlantic conditions

The wet interval recorded between 2850 and 2450 cal a BP (900–500 BC) includes the period of the 'Great Solar Minimum' (Fig. 9; also known as the Homeric climatic Oscillation, or Homeric minimum; Van Geel et al., 1996, 1999). This interval corresponds to a high cosmogenic radionuclide production rate in the atmosphere, related to a weaker shielding against galactic cosmic ray fluxes, producing a steep increase in ¹ the atmosphere (e.g. Reimer et al., 2009) and a rise in radionuclide ¹⁰Be flux (Vonmoos et al., 2006) between ca. 2750 and 2550 cal a вр (800-600 вс). This phase of low solar activity seems to have triggered a climatic change, likely to have been global in extent (e.g. Van Geel et al., 1996; Martin-Puertas et al., 2012), even if this is not as obvious in many archives and could be part of a longer interval of climatic anomaly (e.g. Mayewski et al., 2004). At Lake Pergusa, the climatic expression of the period encompassing the 'Great Solar Minimum' (2850-2450 cal a BP) is a relatively wet interval, as indicated by the $\delta^{18}O_c$ record (Figs 5 and 9). This interval can be recognized in $CaCO_3$ content, $\delta^{13}C_c$ and TOC, and it is accompanied by a pronounced reduction in AP%, which never completely recovers after this interval

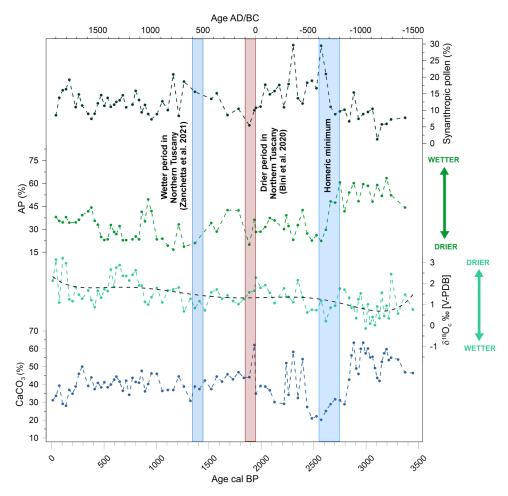


Figure 9. Synanthropic pollen percentage (calculated after Sadori *et al.*, 2013) compared with arboreal pollen percentage (AP) (Sadori *et al.*, 2013), $\delta^{18}O_c$ (this work), and CaCO₃% (this work) for the PG2 core for the last 3500 years. The dotted line for $\delta^{18}O_c$ is a fit of the 6th polynomial order. Highlighted in colored squares are particular chronological intervals discussed in the text. [Color figure can be viewed at wileyonlinelibrary.com]

(Figs. 5 and 9). The reduction in AP%, in the absence of human impact, indicates drier instead of wetter conditions, because the main limiting factor for Mediterranean trees is aridity. Many Greek colonies were founded in Sicily in this period, when there was an unquestionable human impact on vegetation, as already observed by Sadori and Narcisi (2001). The human impact is clearly indicated by the peak in synanthropic pollen (from cultivated plants and weeds/ ruderals favoured by human land use) occurring soon before 2500 cal a вр (550 вс; Fig. 9; Sadori et al., 2013). According to the review by Finné et al. (2019), at ca. 2900 cal a BP (ca. 950 BC; the time interval considered by Finné et al., 2019, is 200 years) wetter conditions seem to have prevailed in southern Italy and in part of the Balkans, but drier conditions were present in the Eastern Mediterranean and in Greece. The unfavourable hydroclimate conditions of Greece and the Eastern Mediterranean and the wetter conditions of Southern Italy (at least in Sicily, also considering the general water deficit of the southern Mediterranean) might have favoured the flourishing of the Greek colony in southern Italy.

However, the Pergusa proxy time series indicates a short period of drier conditions between ca. 2900 and 2800 cal a BP (950–850 BP). Therefore, any climate influence on the settlement of the Greek colony in Southern Italy would need to be confirmed by archives containing higher resolution and more robust chronological data. The coincidence of forest opening (decrease in AP%) when humidity is rising (lower $\delta^{18} O_{\rm c}$) does, however, indicate the presence of a concatenated event.

Following the Late Holocene wet interval, the 'Roman Period' is considered to be characterized by a generally 'benign' climate (the so-called Roman Climatic Optimum lasting between ca. 200 BC and 450 AD, i.e. ca. 2150-1500 cal a BP, e.g. according to Harper, 2017). Surprisingly, the interval between ca. 380 BC and 450 AD (ca. 2330-1500 cal a BP), which has basically marginally higher $\delta^{18}O_c$ compared to the wet interval, does not stand out as a particularly prominent phase of dry conditions of the record (Fig. 9). The interval is set against a trend of increasingly drier conditions, which lasted from ca. 70 BC to 15 AD and subsequently trend towards wetter conditions with lower $\delta^{18}O_c$ in the interval ca. 150–170 AD. We cannot be certain that there is sufficient chronological resolution to fully interpret changes in this interval, but the drier phase occurring at ca. 70 BC to 15 AD followed by a decrease in δ¹⁸O_c resemble the dry-wet phases identified in some speleothem δ¹⁸O records from Corchia, Renella and Rio Martino caves in Central and Northern Italy respectively (Fig. 9; Regattieri et al., 2014; Zanchetta et al., 2016). The wetter interval identified in the speleothem records is associated with an increase in the flood events of the Tiber River, based on historical chronicles (e.g. Aldrete, 2007) and on an increase in floods in northern Tuscany as inferred from archaeological evidence from northern Tuscany (Bini et al., 2020).

A more evident, ca. 250-year wet interval is recognized between ca. 450 and 700 AD (1500—1250 cal a BP), during the late antique—Byzantine times when wetter conditions allowed a period of intense agricultural use of the Sicilian landscape

(Sadori et al., 2016). This period coincides with data from a speleothem δ¹⁸O record from the Apuan Alps in Northern Tuscany, which show a prominent wetter interval during the 6th century AD (Fig. 9; Zanchetta et al., 2021) and is again associated with increasing flood events evidenced from historical sources also in northern Italy (Zanchetta et al., 2021, and references therein). It has been suggested that generally wetter conditions during this period were recognizable in most of the eastern Mediterranean area (e.g. Izedebski et al., 2016). According to Zanchetta et al. (2021) this would correspond to major advection of vapour masses from the Atlantic, and to increasing cyclogenesis over the Mediterranean related to an increase of advection of vapour from Westerlies during winter. This is in agreement with the North Atlantic Oscillation (NAO) negative mode (Fig. 8), as suggested for instance by the NAO reconstruction proposed by Olsen et al. (2012).

 $\delta^{18}O_c$ indicates that drier conditions progressively prevailed after 700 AD (1250 cal a BP), but they are particularly prominent between ca. 1050 and 1450 AD (900-500 cal a BP). This probably represents the regional expression of the Medieval Climatic Anomaly (MCA; Fig. 9; MCA, e.g. Bradley et al., 2003) and this interval, as already highlighted, represents the longest and most prominent arid interval of the last 6700 years of the Pergusa record. This period is consistent with the persistent positive NAO status (Trouet et al., 2009; Olsen et al., 2012; Baker et al., 2015; Fig. 8), which produces a reduction in winter precipitation and generally drier conditions in the western Mediterranean owing to less advection of storms from the Atlantic. According to Roberts et al. (2012), a prominent antiphase between a drier Iberian Peninsula and a wetter Turkey, Greece and Levant is present during this period. Lake Pergusa documents an extension of the influence of drier conditions within the central Mediterranean, as an effect of the positive mode of the NAO (see also Lüning et al., 2019). The wetter interval between ca. 1500 and 1800 AD (450-150 cal a BP) corresponds to the Little Ice Age (LIA; e.g. Mann, 2002). It has been proposed that the western Mediterranean experienced more frequent negative NAO index states during parts of the LIA (e.g. Luterbacher et al., 2006), and Roberts et al. (2012) found a significant antiphase between Mediterranean regions as during the MCA. Figure 8 shows the Pergusa $\delta^{18}O_c$ and NAO index (Olsen et al., 2012). Considering the associated errors in both age models, some important agreement can be observed. In particular, the most prominent correlation is between the mentioned LIA and MCA, but there is also a good correlation for the interval between ca. 2800 and 2400 cal a BP (ca. 800-450 BC) and during the 6th century AD. Therefore, the agreement of the δ¹⁸O_c record with reconstructed NAO index reveals the importance of winter recharge to Lake Pergusa, in addition to the prolonged conditions of summer drought promoting water evaporation.

Long-term hydrological change and fate of Lake Pergusa

In the last 3500 years, across the wetter and drier intervals, there is a clear trend of progressive increase in $\delta^{18}O_c$ values, which suggests a multimillennial trend (Fig. 9). During the Middle–Late Holocene, summer insolation at this latitude has declined and winter insolation has increased progressively (Fig. 8; Berger and Loutre 1991), possibly impacting winter precipitation and lake recharge. An overall decrease in forest cover (lower AP%, Fig. 5) over the same interval would have also produced (especially if promoted by human clearance, as indicated by synanthropic pollen in the last 3000 years, Fig. 9) the so-called catchment effect, where the increasing evaporation of soil water due to land clearance and runoff produced a

long-term increase in $\delta^{18}O_w$. This is expressed by the pollen concentration record, which shows clear evidence of a progressive long-term trend of reduction in the arboreal cover (Sadori and Narcisi, 2001; Sadori et al., 2013). The progressive increase in δ¹⁸O_c was probably accompanied by greater evaporation of lake water with an increase in water salinity (e.g. Fig. 3) due to a combination of long-term natural process (tendency towards progressively reduced recharge and increased evaporation), exacerbated by human activities such as intense land use, evident in the recent past with the substantial increase in lake salinity that occurred in 1988 (Battaglia et al., 1991). This may also explain why, for instance, the interval covering the 'Homeric minimum' was not particularly prominent (<1% change in $\delta^{18}O_c$), with the $\delta^{18}O_c$ signal possibly masked by the unprecedented human impact in the catchment, with a reduction in the arboreal cover and expansion of synanthropic taxa. Considering the evidence of increasing $\delta^{18}O_c$ values over time and the fact that the highest $\delta^{18}O_c$ values have occurred in the last 150 years, we can speculate that the current evidence of a strong increase in salinity and evaporation (Battaglia et al., 1991) is in line with this long-term trend related to climate and human impact. Considering the observed δ¹⁸O_c trend in the Lake Pergusa record, and combined with modelling data, future climate change in the region would probably act to exacerbate the shift to drier conditions (e.g. Giorgi, 2006; Lionello and Scarascia, 2018, 2020) producing an environmental scenario with no precedent in the Holocene history of the lake. It is therefore imperative that local land use management is strategic to support lake hydrology and counter the desiccation of the lake.

However, the correlation of the 'Homeric minimum' with a period of lower δ¹⁸O_c may suggest a more complex fate in the coming decades. It is believed that large changes in solar ultraviolet radiation can indirectly affect climate by inducing atmospheric changes (Van Geel et al., 1999; Gray et al., 2010; Soon et al., 2014). Specifically, it is believed that some centennial-scale climate variability during the Holocene epoch was controlled by variability in the Sun's activity (e.g. Magny, 1993; Van Geel et al., 1999). In particular, a 'great solar minimum' is expected in the near future (2020–2053; e.g. Zharkova 2020). Any reduction in global mean near-surface temperature due to a future decline in solar activity is likely to be a small fraction of projected anthropogenic warming. However, models respond to the solar minimum with patterns in surface pressure and temperature that resemble those of the negative phase of the NAO or Arctic Oscillation (Ineson et al., 2011, 2015). Therefore, set against a trend towards drier conditions, we cannot rule out that the next few decades may experience negative NAO-like modes, with wetter local conditions, moderating the general transition towards drier conditions. However, this would not counteract the long-term trend predicted by the climate models and supported by our results.

Conclusions

The decadal- to centennial-scale palaeolimnological and palaeohydrological reconstruction for Lake Pergusa covering the last 6700 cal a BP indicates the wettest conditions and the highest lake level (even if with possible oscillations) during the first ca. 500–600 years of the record, which is in agreement with previous reconstructions across regional records and obtained in the same lake but at lower resolution (e.g. Sadori and Narcisi, 2001; Zanchetta et al., 2007; Roberts et al., 2008). Progressively drier conditions, in alternation with wetter phases, have developed over the last 6000 years, with a

generally marked trend of drying evident in the last 3000 years. This trend is specifically highlighted by the $\delta^{18}O_c$ record, interpreted here to be mostly driven by summer conditions (as indicated by stable isotope monitoring of contemporary lake water), with a minor control from winter recharge, which may have been affected by the 'amount effect' isotopic signal (Natali *et al.*, 2021).

The $\delta^{18}O_c$ record indicates a generally long period of wetter conditions between ca. 3700 and 2400 cal a BP (1750-450 BC), with a shorter interval of drier conditions (e.g. at ca. 2900 cal a BP - ca. 950 BC). The wetter interval recorded between 2850 and 2450 cal a BP (900–500 BC) by the $\delta^{18}O_c$ record closely overlaps with the period of the 'Great Solar Minimum', which is believed to have produced the so-called Homeric climatic Oscillation (e.g. Van Geel et al., 1996). It corresponds to a dramatic reduction of AP% and increase in synanthropic pollen (Fig. 9), marking the onset of the large-scale Greek colonization of the region. Since then, the pollen record indicates a strong human impact on the environment, and we suggest that this has had a long-term impact also on the hydrological balance of the lake, possibly explaining part of the long-term trends of $\delta^{18}O_c$ in the last 3000 years. Other minor wetter intervals are present at ca. 150 AD, 500-700 AD and during the LIA (ca. 1500-1800 AD in the Pergusa chronology). The longest and driest interval of the record is during the MCA (between ca. 1050 and 1450 AD in the Pergusa chronology), whereas the highest $\delta^{18}O_c$ values are recorded in the last 150 years after the LIA $\delta^{18}O_c$ minimum. This indicates unusually high lake water evaporation in the context of a progressive decrease in precipitation and increase in human impact, moving the lake towards terminal conditions and at a risk of completely drying up, assuming no restoration and protective measures are implemented. The general trend of the last 3000 years suggests that the future climate of the region will experience unprecedented drying, owing to current warming and decreased precipitation. However, the wetter conditions during the Homeric minimum and the LIA, and entry into the 'great solar minimum' in the next few decades (2020-2053; e.g. Zharkova 2020), may suggest that the expected progressive drying caused by current warming may be attenuated over the next few decades, at least at a regional scale, which is of concern. Therefore, it is important not to treat short-term reversals of the long-term drying trend with complacency as action is needed to prevent the hydrological deterioration of Lake Pergusa.

Acknowledgements. Financial support for coring and radiocarbon chronology was provided by the French ANR within the project LAMA (MSHE Ledoux, Besançon, France, project ANR-07-BLAN-0009-01, Michel Magny and Nathalie Combourieu Nebout). Analytical work specific for this paper was supported by Fondi di Ateneo of the University of Pisa (G. Zanchetta and M. Bini) and IGG-CNR. This work is an integration of the targets of the PRIN 2017 'FUTURE Project' (MIUR grant no. 20177TKBXZ_003, Leader G.Z.). We thank the reviewers B. Giaccio and J. Lacey for their constructive comments. Open Access Funding provided by Universita degli Studi di Pisa within the CRUI-CARE Agreement.

Conflicts of interest—The authors declare no conflicts of interest.

Author contributions—Conceptualization G.Z., I.B., M.B., L.S.; data curation G.Z., I.B., M.L., R.T., S.N., F.P.; formal analysis: G.Z., I.B., L.S.; funding acquisition, M.M. G.Z., M.B.; M.B.; investigation: G.Z. I.B., M.M., B.V., M.D.; methodology: G.Z., I.B., M.M., L.S.; project administration: G.Z., M.M.; resources: G.Z., M.M.; software: I.B., M.L., S.N., F.P.; supervision: G.Z., M.B.; validation: I.B., M.M.; visualization: M.B.,

I.B., S.N., M.L., F.P; writing–original draft: G.Z., I.B.; writing, review and editing: M.B., L.S., M.M., B.V., M.D. All authors have read and agreed to the published version of the manuscript.

Supporting information

Additional supporting information can be found in the online version of this article.

Abbreviations. AP%, arboreal pollen %; CAR, cumulative annual rainfall; CMR, cumulative monthly rainfall; DIC, dissolved inorganic carbon; EL, evaporation line; IRMS, isotope ratio mass spectrometer; LIA, Little Ice Age; LMWL, local meteoric water line; MCA, Medieval Climatic Anomaly; NAO, North Atlantic Oscillation; RMA, reduced major axis; TC, total carbon; TIC, total inorganic carbon; TN, total nitrogen; TOC, total organic carbon.

References

Aldrete GS. 2007. Flood of the Tiber in Ancient Rome. Baltimore.

Amore C, Termine R. (eds). 2005. Servizio di monitoraggio ambientale della R. N. S. "Lago di Pergusa" 2003–2004. Sicilia Ambiente S.p.A. Provincia Regionale di Enna.

Amore C, Termine R. (eds). 2007. Servizio di monitoraggio ambientale della R. N. S. "Lago di Pergusa" 2005–2006. Sicilia Ambiente S.p.A., Provincia Regionale di Enna.

Baker A, Hellstrom JC, Kelly BFJ et al. 2015. A composite annualresolution stalagmite record of North Atlantic climate over the last three millennia. Scientific Report 5: 10307. https://doi.org/10.1038/ srep10307

Baneschi I, Magny M, Zanchetta G. 2020. Are stable isotopes of lacustrine carbonate a good tracer of lake hydrology and lake level variability? The Lake Ledro case (Northern Italy). *Alpine and Mediterannean Quarternary* **33**: 99–106.

Bard E, Delaygue G, Rostek F *et al.* 2002. Hydrological conditions in the western Mediterranean basin during the deposition of Sapropel 6 (ca. 175 kyr). *Earth and Planetary Science Letters* **202**: 481–494.

Battaglia M, Cimino A, Gottini V *et al.* 1991. Indagini geofisiche e geochimiche su un lago endoreico della Sicilia: Pergusa. *Bollettino della Società Geologica Italiana* **110**: 53–63.

Bayon G, Dennielou B, Etoubleau J *et al.* 2012. Intensifying weathering and land use in Iron Age Central Africa. *Science* **335**: 1219–1222.

Berger A, Loutre MF. 1991. Insolation values for the climate of the last 10 million years. *Quaternary Science Reviewers* **10**: 297–317.

Bini M, Zanchetta G, Regattieri E *et al.* 2020. Hydrological changes during the Roman Climatic Optimum in Northern Tuscany (Central Italy) as evidenced by speleothem records and archeological data. *Journal Quaternary Science* **35**: 791–802.

Bini M, Zanchetta G, Perșoiu A *et al.* 2019. The 4.2 ka BP Event in the Mediterranean Region: an overview. *Climate of the Past* **15**: 555–577.

Blaauw M. 2010. Methods and code for "classical" age-modelling of radiocarbon sequences. *Quaternary Geochronology* 5: 512–518.

Bowen GJ, Putman A, Brooks JR *et al.* 2018. Inferring the source of evaporated waters using H and O isotopes. *Oecologia* **187**: 1025–1039.

Bradley RS, Hughes MK, Diaz HF. 2003. Climate in Medieval Time. *Science* **302**: 404–405.

Caloiero T, Coscarelli RE, Ferrari E. 2018. Application of the Innovative Trend Analysis Method for the Trend Analysis of Rainfall Anomalies in Southern Italy. *Water Resources Management* **32**: 4971–4983.

Celle-Jeanton H. 2000. Caractérisation Des Précipitations Sur Le Pourtour De La Méditerranée Occidentale—Approche Isotopique Et Chimique. PhD Thesis. Université d'Avignon.

Celle-Jeanton H, Travi Y, Blavoux B. 2001. Isotopic typology of the precipitation in the Western Mediterranean region at three different time scales. *Geophysical Research Letters* **28**: 1215–1218.

- Cerling TE, Quade J. 1993. Stable carbon and oxygen isotopes in soil carbonates. In *Climate Change in Continental Isotopic Records*. In *Geophysical Monograph*, Swart PK, Lohmann KC, McKenzie JA, Savin S (eds). **78**: 217–231.
- Coleman ML, Shepherd TJ, Durham JJ et al. 1982. Reduction of water with zinc for hydrogen isotope analysis. Analytical Chemistry 54: 993–995.
- Craig H. 1961. Isotopic Variations in Meteoric Waters. *Science* **133**: 1702–1703.
- Cramer W, Guiot J, Fader M et al. 2018. Climate change and interconnected risks to sustainable development in the Mediterranean. Nature Climatic Change 8: 972–980.
- Crawford J, Hughes CE, Lykoudis S. 2014. Alternative least squares methods for determining the meteoric water line, demonstrated using GNIP data. *Journal of Hydrology* **519**: 2331–2340.
- Dean JR, Jones MD, Leng MJ et al. 2015. Eastern Mediterranean hydroclimate over the late glacial and Holocene, reconstructed from the sediments of Nar lake, central Turkey, using stable isotopes and carbonate mineralogy. *Quaternary Science Reviews* **124**: 162–174.
- Epstein S, Mayeda T. 1953. Variations of oxygen-18 of waters from natural sources. *Geochimica et Cosmochimica Acta* 4: 213–224.
- Francke A, Wagner B, Just J *et al.* 2016. Sedimentological processes and environmental variability at Lake Ohrid (Macedonia, Albania) between 637 ka and the present. *Biogeosciences* **13**: 1179–1196.
- Finné M, Woodbridge J, Labuhn I, Roberts CN. 2019. Holocene hydro-climatic variability in the Mediterranean: A synthetic multiproxy reconstruction. *The Holocene* **29**: 847–863.
- Gat JR. 1996. Oxygen and hydrogen isotopes in the hydrological cycle. *Annual Review Earth Planetary Science* **24**: 225–262.
- Gat JR, Carmi I. 1970. Evolution of the isotopic composition of atmospheric waters in the Mediterranean Sea area. *Journal Geophysical Research* **75**: 3039–3048.
- Grasso M, Amore C, Maniscalco R et al. 2003. Dati preliminari sulle ricerche stratigrafiche e sedimentologiche eseguite nel Lago di Pergusa (Enna). Bollettino dell'Accademia Gioenia di Scienze Naturali 36: 173–190.
- Giorgi F. 2006. Climate change hot spots. Geophysical Research Letters 33: L08707.
- Giustini F, Brilli M, Patera A. 2016. Mapping oxygen stable isotopes of precipitation in Italy. *Journal of Hydrology, Reg. Stud* 8: 162–181.
- Gray LJ, Beer J, Geller M, Haigh JD et al. 2010. Solar influence on climate. Review of Geophysics 48: RG4001.
- Gu B, Schelske CL, Hodell DA. 2004. Extreme ¹³C enrichment in a shallow hypereutropic lake: Implications for carbon cycling. *Limnology and Oceanography* **49**: 1152–1159.
- Harper K. 2017. The Fate of Rome. Climate, Disease and the End of an Empire. Princeton University Press: Princeton and Oxford.
- Hollander DJ, McKenzie JA. 1991. CO₂ control on carbon-isotope fractionation during aqueous photosynthesis: A paleo-pCO₂ barometer. *Geology* **19**: 929–932.
- IAEA/WMO, 2020. Global Network of Isotopes in Precipitation. The GNIP Database. Accessible at: http://www.iaea.org/water
- Ineson S, Scaife AA, Knight JR *et al.* 2011. Solar forcing of winter climate variability in the Northern Hemisphere. *Nature Geosciences* 4: 753–757
- Ineson S, Maycock AC, Gray LJ *et al.* 2015. Regional climate impacts of a possible future grand solar minimum. *Nature Communications* **6**: 7535
- Isola I, Zanchetta G, Drysdale RN. 2019. The 4.2 ka event in the central Mediterranean: new data from a Corchia speleothem (Apuan Alps, central Italy). *Climate of the Past* **15**: 135–151.
- Ito E. 2001. Application of stable isotope techniques to inorganic and biogenic carbonates. In *Tracking Environmental Change Using Lake Sediments, Vol. 2, Physical and Geochemical Methods,* Last WM, Smol JP (eds). Kluwer: Dordrecht; 351–371.
- Izedebski A, Pickett J, Roberts N *et al.* 2016. The environmental, archaeological and historical evidence for regional climatic changes and their societal impacts in the Eastern Mediterranean in Late Antiquity. *Quaternary Science Reviews* **136**: 189–208.
- Kelly EF, Chadwik OA, Hilinski TE. 1998. The effect of plant in mineral weathering. *Biogeochemistry* **42**: 21–53.
- Lacey JH, Leng JM, Francke A et al. 2016. Northern Mediterranean climate since the Middle Pleistocene: a 637 ka stable isotope record

- from Lake Ohrid (Albania/Macedonia). *Biogesciences* 13: 1801–1820.
- Leng MJ, Marshall JD. 2004. Palaeoclimate interpretation of stable isotope data from lake sediment archives. *Quaternary Science Reviews* **23**: 811–831.
- Leng MJ, Baneschi I, Zanchetta G *et al.* 2010a. Late Quaternary palaeoenvironmental reconstruction from Lakes Ohrid and Prespa (Macedonia/Albania border) using stable isotopes. *Biogeosciences* 7: 1347–1359.
- Leng MJ, Jones MD, Frogley MR, Eastwood WJ *et al.* 2010b. Detrital carbonate influences on bulk oxygen and carbon isotope composition of lacustrine sediments from the Mediterranean. *Global and Planetary Change* **71**: 175–182.
- Leng MJ, Wagner B, Boehm A *et al.* 2013. Understanding past climatic and hydrological variability in the Mediterranean from Lake Prespa sediment isotope and geochemical record over the Last Glacial cycle. *Quaternary Science Review* **66**: 123–136.
- Leone G, Leoni L, Sartori F. 1988. Revisione di un metodo gasometrico per la determinazione di calcite e dolomite. *Atti Società Toscana di Scienze Naturali Memorie Serie A* **95**: 7–20.
- Lionello P, Scarascia L. 2018. The relation between climate change in the Mediterranean region and global warming. *Regional Environmental. Change* **18**: 1481–1493.
- Lionello P, Scarascia L. 2020. The relation of climate extremes with global warming in the Mediterranean region and its north versus south contrast. *Regional Environmental Change* **20**: 31. https://doi.org/10.1007/s10113-020-01610-z
- Liotta M, Favara R, Valenza M. 2006. Isotopic composition of the precipitations in the central Mediterranean: origin marks and orographic precipitation effects. *Journal of Geophysical Research* 111: 19302.
- Liotta M, Grassa F, D'Alessandro W *et al.* 2013. Isotopic composition of precipitation and groundwater of Sicily, Italy. *Applied Geochemistry* **34**: 199–206.
- Lohmann KC. 1988. Geochemical patterns of meteoric diagenetic system and their application to study paleokarst. In "Paleokarst", chapter 2, James NP, Coquette PW (eds). Springer-Verlag: New York; 58–80.
- Lüning S, Schulte L, Garcés-Pastor S et al. 2019. The Medieval Climate Anomaly in the Mediterranean region. *Paleoceanography and Paleoclimatology* **34**: 1625–1649.
- Luterbacher J et al. 2006. Ch. 1 Mediterranean climate variability over the last centuries: a review. In *The Mediterranean Climate: An Overview of the Main Characteristics and Issues*, Lionello P, Malanotte-Rizzoli P, Boscolo R (eds). Elsevier: Netherlands; 27–148.
- Magny M. 1993. Solar influences on Holocene climatic changes illustrated by correlations between past lake-level fluctuations and the atmospheric ¹⁴C. *Quaternary Research* **40**: 1–9.
- Magny M, Vanniére B, Calo C *et al.* 2011. Holocene hydrological changes in south-western Mediterranean as recorded by lake-level fluctuations at Lago Preola, a coastal lake in southern Sicily, Italy. *Quaternary Science Reviews* **30**: 2459–2475.
- Magny M, Vanniere B, Zanchetta G *et al.* 2009. Possible complexity of the climatic event around 4300–3800 cal. BP in the central and western Mediterranean. *The Holocene* **19**: 1–11.
- Magny M, Combourieu-Nebout N, de Beaulieu JL *et al.* 2013. North–south palaeohydrological contrasts in the central Mediterranean during the Holocene: tentative synthesis and working hypotheses. *Climate of the Past* **9**: 2043–2071.
- Mann T. 2002. *The Little Ice Age*. In: Dr Michael C MacCracken and Dr John S Perry (eds) Encyclopedia of Global Environmental Change. Vol. 1, 1-6.
- Mannella G, Zanchetta G, Regattieri E. 2020. Effects of organic removal techniques prior to carbonate stable isotope analysis of lacustrine marls: A case study from palaeo-lake Fucino (central Italy). *Rapid Communications in Mass Spectrometry* **34**: e8623.
- Marchina C, Zuecco G, Chiogna G *et al.* 2020. Alternative methods to determine the δ^2 H- δ^{18} O relationship: An application to different water types. *Journal fo Hydrology* **587**: 124951.
- Martin-Puertas C, Matthes K, Brauer A *et al.* 2012. Regional atmospheric circulation shifts induced by a grand solar minimum. *Nature Geoscience* **5**: 397–401.

- Mayewski PA, Rohling EE, Stafer JC et al. 2004. Holocene climate variability. Quaternary Research 62: 243–255.
- Meyers PA. 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology* **114**: 289–302.
- Meyers PA. 2003. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. *Organic Geochemistry* **34**: 261–289.
- Meyers PA, Ishiwatari R. 1993. The early diagenesis of organic matter in lacustrine sediments. In *Organic Geochemistry*, Engel M, Macko SA (eds). Plenum: New York; 185–200.
- Natali S, Baneschi I, Doveri M et al. 2021. Meteorological and geographical control on stable isotope signature of precipitation in a western Mediterranean area (Tuscany, Italy): disentangling a complex signal. *Journal of Hydrology* 603: 126944.
- Oehlerich M, Braumer M, Lücke A *et al.* 2013. Effects of organic matter on carbonate stable isotope ratios (δ¹³C, δ¹⁸O values)– Implication for analyses of bulk sediments. *Rapid Communication Mass Spectrometry* **27**: 707–712.
- Olsen J, Anderson NJ, Knudsen MF. 2012. Variability of the North Atlantic Oscillation over the past 5,200 years. *Nature Geoscience* 5: 808–812.
- Pappalardo G, Ferrara V, Rapisarda F et al. 2006. Groundwater interaction with endoreic lake: effects on the ecological system of the Pergusa Lake, central-eastern Sicily, Italy. In Kovar K., Hrkal Z., Bruthans J. (eds.), 2006. Proceedings of the HydroEco '2006–International Conference on Hydrology and Ecology: the Groundwater/Ecology Connection, Karlovy Vary, Czech Republic, 11-14 September 2006 (pp. 362). Czech Republic: Czech Association of Hydrogeologists. OCLC n. 858663430.
- Regattieri E, Zanchetta G, Drysdale RN *et al.* 2014. Lateglacial to Holocene trace element record (Ba, Mg, Sr) from Corchia Cave (Apuan Alps, central Italy): paleoenvironmental implications. *Journal of Quaternary Science* **29**: 381–392.
- Reimer PJ *et al.* 2009. Intcal09 and Marine09 radiocarbon age calibration curves, 0-50,000 years cal bp. *Radiocarbon* **51**: 1111–1150.
- Roberts N, Jones MD, Benkaddur A *et al.* 2008. Stable isotope records of Late Quaternary climate and hydrology from Mediterranean lakes: the ISOMED synthesis. *Quaternary Science Review* **27**: 2426–2441.
- Roberts N, Moreno A, Valero-Garcés BL et al. 2012. Palaeolimnological evidence for an east–west climate see-saw in the Mediterranean since AD 900. Global and Planetary Change 84–85: 23–34.
- Roberts CN, Zanchetta G, Jones MD. 2010. Oxygen isotopes as tracers of Mediterranean climate variability: an introduction. *Global and Planetary Change* **71**: 135–140.
- Rozanski K, Araguás-Araguás L, Gonfiantini R. 1993. Isotopic patterns in Global Precipitation. In *Climate Change in Continental Isotopic Records Geophysical Monograph*. Swart PK, Lohmann KC, McKenzie JA, Savin S (eds). **78**: 1–36.
- Sadori L, Narcisi B. 2001. The Postglacial record of environmental history from Lago di Pergusa. Sicily. The Holocene 11: 655–670.
- Sadori L, Ortu E, Peyron O, Zanchetta G, Vannière B, Desmet M, Magny M. 2013. The last 7 millennia of vegetation and climate changes at Lago di Pergusa (central Sicily, Italy). Climate of the Past 9: 1969–1984.
- Sadori L, Giraudi G, Masi A et al. 2016. Climate, environment and society in southern Italy during the last 2000 years. A review of the environmental, historical and archaeological evidence. Quaternary Science Reviews 136: 173–188.
- Sadori L, Zanchetta G, Giardini M. 2008. Last Glacial to Holocene palaeoenvironmental evolution at Lago di Pergusa (Sicily, Italy) as inferred by pollen, microcharcoal, and stable isotopes. *Quaternary International* **181**: 4–14.
- Salvati L, Bajocco S. 2011. Land sensitivity to desertification across Italy: Past and future. *Applied Geography* **31**: 223–231.
- Stuiver M, Reimer PJ, Reimer RW. 2021. CALIB 8.2 [WWW program] at http://calib.org, accessed 2021-4-3.

- Soon W, Velasco Herrera VM, Selvaraj K *et al.* 2014. A review of Holocene solar-linked climatic variation on centennial to millennial timescales: Physical processes, interpretative frameworks and a new multiple cross-wavelet transform algorithm. *Earth-Science Reviews* 134: 1–15.
- Talbot MR. 1990. A review of the paleohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates. *Chemical Geology* **80**: 261–279.
- Teranes JL, Mckenzie JA, Bernasconi SM *et al.* 1999. A study of oxygen isotopic fractionation during bio-induced calcite precipitation in eutrophic Baldeggersee, Switzerland. *Geochim. Cosmochim. Acta* **63**: 1981–1989.
- Termine R. 2006. La Riserva Naturale Speciale del lago di Pergusa. I luoghi, il percorso didattico, la flora, la fauna, le schede, il regolamento d'uso, gli elenchi floro-faunistici. Città Aperta Edizioni, Troina (Enna).
- Trouet VR, Esper J, Graham NE *et al.* 2009. Persistent positive North Atlantic Oscillation Mode dominated the Medieval Climate Anomaly. *Science* **324**: 78–80.
- Van Geel B, Buurman J, Waterbolk HT. 1996. Archaeological and palaeoecological indications of an abrupt climate change in The Netherlands, and evidence for climatological teleconnections around 2650 bp. *Journal Quaternary Sciences* 11: 451–460.
- Van Geel B, Raspopoy OM, Renssen H et al. 1999. The role of solar forcing upon climate change. Quaternary Science Reviews 18: 331–338.
- Vonmoos M, Beer J, Muscheler R. 2006. Large variations in Holocene solar activity: Constraints from ¹⁰Be in Greenland Ice Core Project ice core. *Journal Geophysical Research* **111**: A10105.
- Weiss H. 2016. Global megadrought, societal collapse and resilience at 4.2–3.9 ka BP across the Mediterranean and west Asia. *Clim. Chang. Cult. Evol. PAGES Mag* **24**: 62–63.
- Whittington G, Edwards KJ, Zanchetta G *et al.* 2015. Lateglacial and early Holocene climates of the Atlantic margins of Europe: stable isotope, mollusk and pollen records from Orkney, Scotland. *Quaternary Science Reviews* **122**: 112–130.
- Wierzbowski H. 2007. Effects of pre-treatments and organic matter on oxygen and carbon isotope analyses of skeletal and inorganic calcium carbonate. *International Journal of Mass Spectrometry* **268**: 16–29.
- Zanchetta G, Bini M, Bloomfield K, Izdebski A *et al.* 2021. Beyond one-way determinism: San Frediano's Miracle and Climate Change in Central and Northern Italy in Late Antiquity. *Climatic Change* **165**: 25.
- Zanchetta G, Baneschi I, Francke A *et al.* 2018. Evidence for carbon cycling in a large freshwater lake in the Balkans over the last 0.5 million years using the isotopic composition of bulk organic matter. *Quaternary Science Reviews* **202**: 154–165.
- Zanchetta G, Bonadonna FP, Leone G. 1999. A 37-meter record of paleoclimatological events from stable isotope data on molluscs in Valle di Castiglione, near Rome, Italy. *Quaternary Research* **52**: 293–299
- Zanchetta G, Regattieri E, Isola I *et al.* 2016. The so-called "4.2 event" in the central Mediterranean and its climatic teleconnections. *Alpine and Mediterranean Quaternary* **29**: 5–17.
- Zanchetta G, Borghini A, Fallick AE *et al.* 2007. Late Quaternary palaeohydrology of Lake Pergusa (Sicily, southern Italy) as inferred by stable isotopes of lacustrine carbonates. *Journal of Paleolimnology* **38**: 227–239.
- Zanchetta G, van Welden A, Baneschi I *et al.* 2012. Multiproxy record for the last 4500 years from Lake Shkodra (Albania/Montenegro). *Journal of Quaternary Science* 27: 780–789.
- Zielhofer C, Fletcher WJ, Mischke S *et al.* 2017. Atlantic forcing of Western Mediterranean winter rain minima during the last 12,000 years. *Quaternary Science Reviews* **157**: 29–51.
- Zharkova V. 2020. Modern Grand Solar Minimum will lead to terrestrial cooling. *Temperature* **7**: 217–222.