Research paper

The Holocene
22(10) 1135–1142

Reprints and permission:
sagepub.co.uk/journalsPermissions.nav
DOI: 10.1177/0959683612441841
hol.sagepub.com
SAGE

Elemental (C/N ratios) and isotopic ($\delta^{15}N_{org}$, $\delta^{13}C_{org}$) compositions of sedimentary organic matter from a high-altitude mountain lake (Meidsee, 2661 m a.s.l., Switzerland): Implications for Lateglacial and Holocene Alpine landscape evolution

Florian Thevenon,[1] Thierry Adatte,[2] Jorge E Spangenberg[2] and Flavio S Anselmetti[3]

Abstract
The deposition of Late Pleistocene and Holocene sediments in the high-altitude lake Meidsee (located at an altitude of 2661 m a.s.l. in the Southwestern Alps) strikingly coincided with global ice-sheet and mountain-glacier decay in the Alpine forelands and the formation of perialpine lakes. Radiocarbon ages of bottom-core sediments point out (pre-) Holocene ice retreat below 2700 m a.s.l., at about 16, 13, 10, and 9 cal. kyr BP. The Meidsee sedimentary record therefore provides information about the high-altitude Alpine landscape evolution since the Late Pleistocene/Holocene deglaciation in the Swiss Southwestern Alps. Prior to 5 cal. kyr BP, the C/N ratio and the isotopic composition of sedimentary organic matter ($\delta^{15}N_{org}$, $\delta^{13}C_{org}$) indicate the deposition of algal-derived organic matter with limited input of terrestrial organic matter. The early Holocene and the Holocene climatic optimum (between 7.0 and 5.5 cal. kyr BP) were characterized by low erosion (decreasing magnetic susceptibility, χ) and high content of organic matter (C_{org} > 13 wt.%), enriched in $^{13}C_{org}$ (> −18‰) with a low C/N (~10) ratio, typical of modern algal matter derived from in situ production. During the late Holocene, there was a long-term increasing contribution of terrestrial organic matter into the lake (C/N > 11), with maxima between 2.4 and 0.9 cal. kyr BP. A major environmental change took place 800 years ago, with an abrupt decrease in the relative contribution of terrestrial organic material into the lake compared with aquatic organic material which subsequently largely dominated (C/N drop from 16 to 10). Nonetheless, this event was marked by a rise in soil erosion (χ), in nutrients input (N and P contents) and in anthropogenic lead deposition, suggesting a human disturbance of Alpine ecosystems 800 years ago. Indeed, this time period coincided with the migration of the Walser Alemannic people in the region, who settled at relatively high altitude in the Southwestern Alps for farming and maintaining Alpine passes.

Keywords
aquatic productivity, deglaciation, lake sediments, Southwestern Alps, stable isotopes, terrestrial organic matter

Received 5 October 2011; revised manuscript accepted 18 January 2012

Introduction

Open questions remain for Holocene paleoclimate about the timing of the last deglaciation in the Alps and the associated environmental changes (Schlüchter, 1988) subsequent to the maximum ice extent during the Last Glacial Maximum (LGM, from about 24,000 to 21,000 calendar years Before Present (cal. kyr BP)). The reconstructions of the LGM ice-surface elevations and ice-flow directions, which are based on field mapping of glacial trimlines, ice-erosional features and periglacial geomorphology (e.g. Kelly et al., 2006), implies an ice thickness of > 1400 m and a surface elevation of > 3000 m for the LGM of the southern Valais (Southern Switzerland) ice field (Kelly et al., 2004). Nevertheless, some radiocarbon dates of organic lacustrine sediments from peri- and inner-Alpine regions (i.e. from lake sediments deposited subsequently to the LGM) suggest that the decrease in ice volume and the retreat of the last Alpine glacier system extending to the forelands could have lasted as little as a few hundred years (Lister, 1988; Schlüchter, 1988). This interpretation is corroborated by surface exposure dating of bedrock and erratic blocks using cosmogenic nuclides (e.g. ^{10}Be), which indicate (1) a ~21 cal. kyr BP age of the onset of the deglaciation when the Rhône glacier abandoned the terminal moraines on the northern Alpine foreland (Ivy-Ochs et al., 2004) but also

[1]University of Geneva, Switzerland
[2]University of Lausanne, Switzerland
[3]Eawag, Swiss Federal Institute of Aquatic Science and Technology, Switzerland

Corresponding author:
Florian Thevenon, Institute F.-A. Forel, University of Geneva, Versoix, Switzerland.
Email: Florian.Thevenon@yahoo.fr

(2) Alpine glacial advances ~16 cal. kyr BP, at the onset of the Younger Dryas (~12 cal. kyr BP), ~11 and 8 cal. kyr BP, and during the 'Little Ice Age' (LIA; ~0.6–0.2 cal. kyr BP) (Holzhauser et al., 2005; Ivy-Ochs et al., 2006).

The timing of the onset of ice decay can be alternatively inferred by dating the earliest time of alpine soils formation. For instance, radiocarbon dating of the most refractory organic matter (OM) from an Alpine environment of northern Italy (2100 m above sea level; a.s.l.) gives the highest ages of up to 17 cal. kyr BP (Favilli et al., 2008). By comparison, the radiocarbon dating and the pollen analyses of the oldest sediment from foreland lakes (e.g. Constance, Zurich, and Neuchatel) locate their earliest formation around 17.5 cal. kyr BP (synthesis in Ivy-Ochs et al., 2004). The study of geological and biological materials from lacustrine sediments that have *accumulated since* the deglaciation furthermore allows to reconstruct the landscape response to global climate changes (e.g. Lake Geneva; Girardclos et al., 2005). Additional advantages of studying high-altitude lakes from the Alpine region are that (1) these ecosystems have been only recently impacted by human activities, and (2) the altitude and the Alpine topography tend to amplify the temperature anomalies, as demonstrated by a higher climate warming during the 20th century in the European Alps (Beniston, 2006).

The type and amount of sedimentary OM can be used to reflect past fluctuations in lakes' productivity and terrestrial inputs linked to climate-induced environmental changes (Leng and Marshall, 2004; Meyers, 1997; Talbot and Johannessen, 1992). Indeed, land-derived OM has C/N ratio higher than 14–20, while phytoplankton and aquatic macrophytes exhibit C/N ratios between 4 and 10 (Meyers and Teranes, 2001). The carbon and nitrogen stable-isotope composition of autochtonous sedimentary OM can also be used to reconstruct changes in aquatic productivity rates and sources of nutrients (Bertrand et al., 2009). This is due to the fact that during periods of enhanced aquatic productivity, lacustrine algae preferentially consumes the dissolved light carbon isotope (^{12}C) during photosynthesis. The enhanced uptake of $^{12}CO_2$ by aquatic organisms results in the production and the sedimentation of ^{13}C-poor OM, i.e. with more negative $\delta^{13}C_{org}$ ($^{13}C/^{12}C$ ratio) values (Meyers and Teranes, 2001). Lower $\delta^{13}C$ values of sedimentary OM can also reflect increased influx of terrestrial OM into the lake, or increased dissolved CO_2 supply to the lake water owing to a reduction in the seasonal ice cover (enhanced exchange between the atmosphere and the lake water) or changes in the lake trophic levels (Harwart et al., 1999; Teranes and Bernasconi, 2005). For the same reasons, longer and stronger lake stratification or enhanced photosynthesis by aquatic plants and algae may also influence the $\delta^{15}N_{org}$ (^{14}N and ^{15}N discrimination during N fixation) composition of lacustrine OM (Lu et al., 2010; Xu et al., 2006).

This study aims to reconstruct the climate-induced environmental changes that occurred since the LGM in the Southern Alps, by studying a well-dated organic-rich sediment sequence (121 cm long) from Meidsee (Southern Alps, Switzerland), which was deposited during the Late Pleistocene and Holocene in a pristine landscape at high altitude (2661 m a.s.l.). Previous studies of heavy-metal record (including Pb isotopes) from this archive demonstrated the long-range transport of European air pollutants and the strong impact of the mining activities during the Roman Empire and the European Industrial Revolution (Thevenon et al., 2011). In this study, we further investigate the concentration and the isotopic composition of the sedimentary OM, in an attempt to reconstruct the Alpine landscape response to the long-term climatic changes following the deglaciation and during the Holocene. Organic geochemical data, including organic carbon concentration (C_{org}), nitrogen content (N), C/N atomic ratios, phosphorus content (P), and carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N_{org}$) isotope ratios, are compared with magnetic susceptibility, in order to determine the sources of OM and their possible variations through time with respect to climate-induced environmental changes.

Study site, sediment coring and core chronology

Meidsee

The small high-alpine Meidsee is located in the Swiss Alps at 2661 m a.s.l. on the western shoulder of the Turtmann Valley, a southern tributary to the Rhône Valley and the westernmost German-speaking valley (Canton of Valais). The lake is located less than 1 km from Meidpass (2790 m a.s.l.) which connects the Turtmann and Rhône valleys to the foot of the Southern Alps and the Mediterranean countries. The lake has a roundish shape with a diameter of ~200 m and a maximum water depth of ~15 m (Figure 1a and b). It has no permanent inflow and thus receives reduced detrital sediment supply. Its non-glaciated catchment covers less than 0.5 km^2 and consists of crystalline rocks and relatively thin soils (10–50 cm). The lake is at least partially frozen during almost 6 months per year. During summer months, macroalgae are observed on the northwestern part of the lake at about 1–2 m water depth (Figure 2a).

Seismic survey and sediment coring

In September 2009, a reflection seismic survey was conducted followed on the same day by collection of a series of gravity short cores. The seismic source/receiver assembly consisted of a GEO-ACOUSTIC pinger system (3.5 kHz) operated from an inflatable boat on a pushed catamaran using regular GPS navigation. A dense grid of 10 × 10 lines was acquired. Seismic data were stored digitally in SEG-Y format, filtered (2–6 kHz) and loaded in KINGDOM SUITE software for interpretation. A bathymetric map was established on the basis of the interpolated seismic data (Figure 1b). Reflection seismic profiles showed at the base of seismic penetration a strong reflection of an acoustic basement with rugged morphology that represents the irregular top of the bedrock or the ground moraine (Figure 1c). In the deepest area, the acoustic basement is overlain by an up to 1.5 m thick succession of very low-amplitude reflections characterized by moderate layer continuity (Figure 1c). These reflections form onlaps onto the acoustic basement and wedge out at water depths of ~10 m. This low-amplitude seismic sequence is barely to be discerned from the water body and thus represents low-impedance lacustrine sediments, which were cored with five gravity short cores (6 cm diameter) near the deepest area. Core ME09-5 (121 cm long) was used for this study.

Terrestrial and aquatic modern organic matter sources (Table 1 and Figure 2)

In order to constrain the elemental and isotopic compositions of modern terrestrial and aquatic sources of sedimentary organic matter in Meidsee, a sampling campaign was conducted in the small watershed of the lake in August 2011. Macroalgae were collected in the northwestern part of the lake (sample A on Figure 2a) where water depth was about 1–2 m. A ~1 m long coring tube left during two years in the northern part of the lake where water depth was about 1–2 m, allowed the collection of modern lacustrine organic matter derived from in situ production (sample T on Figure 2h). Three terrestrial plant samples (H1 to H3 on Figure 2), two lichen samples (samples L1 and L2 on Figure 2), and one surface soil sample (sample S on Figure 2d) were also collected, as well as animal excrements (sample W on Figure 2f) that were abundant in the catchment because of summer cattle grazing (goat and sheep).

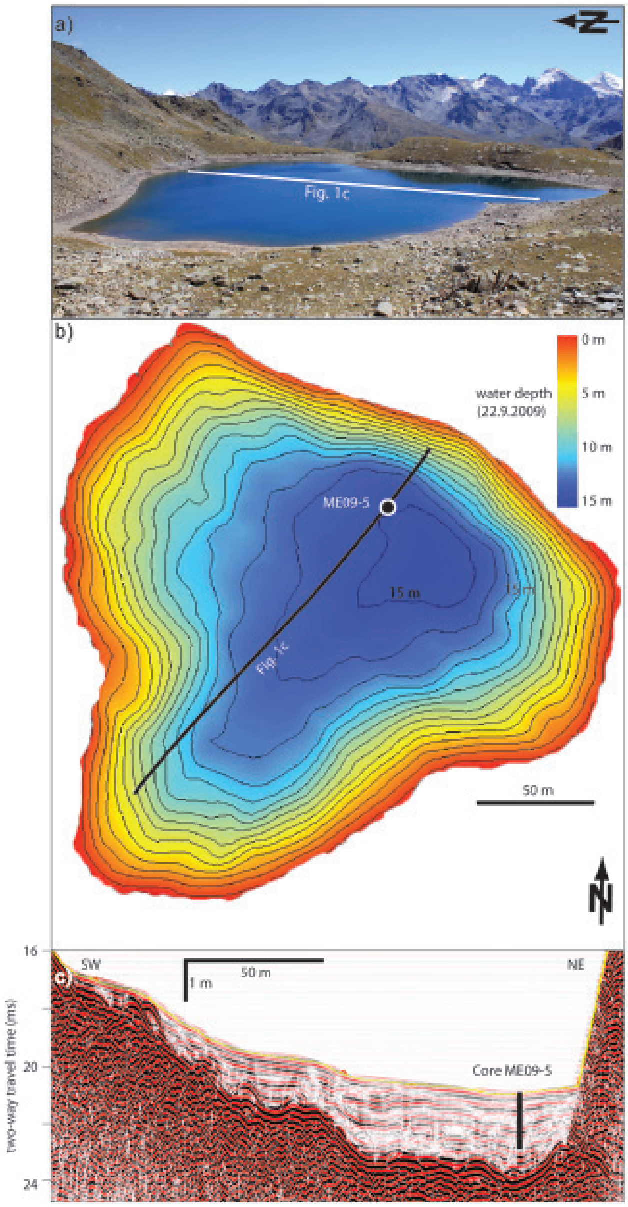

Figure 1. (a) Photo of Meidsee in summer 2011 showing a relatively low water-depth. (b) Bathymetric map of Meidsee constructed with interpolated grid (10 × 10 lines) of seismic data acquired in 2009. Black line represents location of seismic line shown in (c) and dots indicate location of core used for this study. (c) 3.5 kHz seismic line showing low-amplitude seidmentary unit reaching a maximum thickness of 1.5 m focusing in the basin. Coring location and penetration is indicated by vertical black bar. The water column has been partly muted for better visibility of sedimentary sequence.

Methods

Magnetic susceptibility (χ) and core sampling

Magnetic susceptibility (χ) was measured with a GEOTEK multi-sensor core-logger at ETH Zurich with a sampling interval of 5 mm. Afterwards, the core was split, photographed, described macroscopically and sampled continuously at 1 cm intervals. The sediment samples, as well as the terrestrial and aquatic modern samples, were frozen, freeze-dried and grounded by hand in agate mortar, and homogenized to a fine powder for the subsequent geochemical analyses.

Phophorus (P) analysis

Total phosphorus (P) analyses were performed on ~100 mg of dry powdered sediment, mixed with 1 ml of MgNO3 and left to dry in an oven at 45°C for 2 h. The samples were then heated in a furnace at 550°C for 2 h. After cooling, 10 ml of 1N HCl were added and placed under constant shaking for 14 h. The solutions were filtered with a 63 µm filter, diluted ten times, and analyzed using the ascorbic acid method of Eaton et al. (1995). For this process, the solution was mixed with ammonium molybdate and potassium antimonyl tartrate to form phosphomolybdic acid. The intensity of the blue color of this acid measured (three times with a precision better than 5%) with a photospectrometer (Perkin Elmer UV/Vis Photospectrometer Lambda 10) was finally converted to the concentration of PO_4 in mg/l.

Organic carbon (C_{org}) and nitrogen (N) contents, and isotope analyses of the organic matter ($\delta^{13}C_{org}$ and $\delta^{15}N_{org}$)

Total organic carbon content (C_{org}), total nitrogen concentration (%N), and C_{org} and N isotope compositions were determined by flash combustion on a Carlo Erba 1108 elemental analyzer (EA) connected to a Thermo Fisher Scientific Delta V isotope ratio mass spectrometer (IRMS) that was operated in the continuous helium flow mode via a Conflo III split interface (EÃIRMS). An aliquot of the sample was wrapped in a tin capsule and combustion was done in an O_2 atmosphere in a quartz reactor at 1020°C packed with Cr_2O_3 and $(Co_3O_4)Ag$ to form CO_2, N_2, NO_x and H_2O. The gases were then passed through a reduction reactor containing elemental copper and copper oxide at 640°C to remove excess O_2 and to reduce the non-stoichiometric nitrous products (NO_x) to N_2. Water was subsequently removed by anhydrous $Mg(ClO_4)_2$. N_2 and CO_2 were then separated in a packed gas chromatographic column (Pora-PLOT Q, 5 m length, 1/4 inch i.d.) at 70°C, and analyzed for their isotopic composition on the IRMS. Pure N_2 and CO_2 gases were inserted in the He carrier flow as pulses of standard gases. The $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ values are reported relative to the Vienna Pee Dee Belemnite standard (VPDB) and air-N_2, respectively. The calibration and assessment of the reproducibility and accuracy of the isotopic analysis were based on replicate analyses of laboratory standard materials and international reference materials. The reproducibility was better than 0.1‰ for both carbon and nitrogen.

Results and discussion

Sediment-core lithology

The sediment cores consist of a fine-grained, low-density (1.0–1.1 g/cm^3; Thevenon et al., 2011) dark-colored organic-rich gyttja. Only faint laminations can be discerned. In the lower part (114 cm core-depth) and in the upper part (23 cm core-depth) of the sediment core, the χ slightly increases and ~1 cm thick light-colored layers occur (Figures 3 and 4). X-ray analyses demonstrate that these two layers are enriched in well-crystallized minerals, especially phyllosilicates (mica and chlorite), reflecting higher detrital input. SEM observations of the oldest sediments reveal the abundance of phytoplankton which also compose the modern aquatic OM (diatoms, dinoflagellate, and spores; Figures 2j and k). This result points out sustained input of algal matter derived from in situ production to Meidsee sediment, from the deglaciation to present.

Meidsee chronostratigraphy

The age model of core ME09-05 has been previously published in detail in Thevenon et al. (2011), showing a reservoir age of ~1650 years possibly because of the input of stable and old refractory organic matter present in Alpine soils and a long water residence time (Egli et al., 2009; Harwart et al., 1999). Here, the depth–age model was presented in calendar years Before Present (cal. yr BP), where present is AD 2010 (Figure 3). The occurrence of

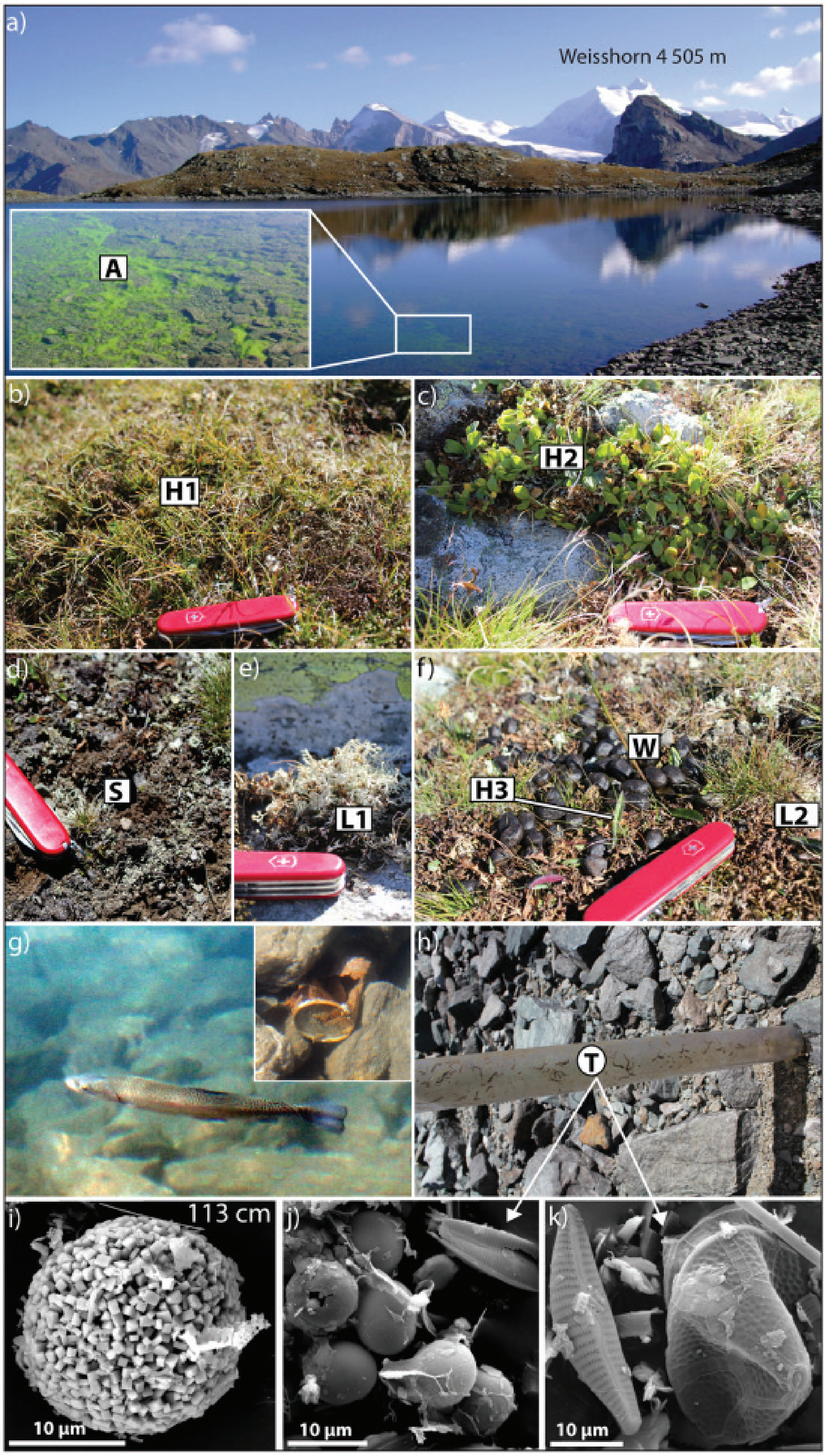

Figure 2. Terrestrial and aquatic modern organic matter sources sampled in the small watershed of Meidsee in summer 2011. The macroalgae (sample A on (a)) were collected in the northwestern part of the lake. Three herbaceous samples (samples H1 to H3 on (b), (c) and (f)), one surface soil sample (sample S on (d)), two lichen samples (samples L1 and L2 on (e) and (f)), and animal excrements (sample W on (f)) were also sampled. A ~1 m long coring tube (sample T on (h)) left in the northern part of the lake in summer 2009 (a), when water depth was about 1–2 m higher than in summer 2011 (a), allowed the collection of modern particulate lacustrine organic matter. SEM image of sample T (j and k) and of pyrite framboids from sediment sampled at 113 cm.

Table 1. C/N ratios and organic $\delta^{13}C$ compositions of different types of modern aquatic (upper part) and terrestrial (lower part) sources of organic matter to sediments of Meidsee.

Sample label	Organic matter source	C/N	Mean $\delta^{13}C_{org}$ (‰ vs PDB)	SD $\delta^{13}C_{org}$	*n*
A	Macroalgae	14.88	−15.6	0.99	3
T	Mixed plankton	10.86	−14.1	1.02	3
H1	Herbaceous	24.68	−27.8	0.61	2
H2	Herbaceous	25.82	−24.7	0.33	2
H3	Herbaceous	19.49	−28.1	0.05	3
L1	Lichen	63.55	−25.0	0.02	2
L2	Lichen	65.73	−24.5		1
S	Surface soil	16.99	−25.1	0.12	3
W	Animal excrement	21.54	−28.4	0.35	2

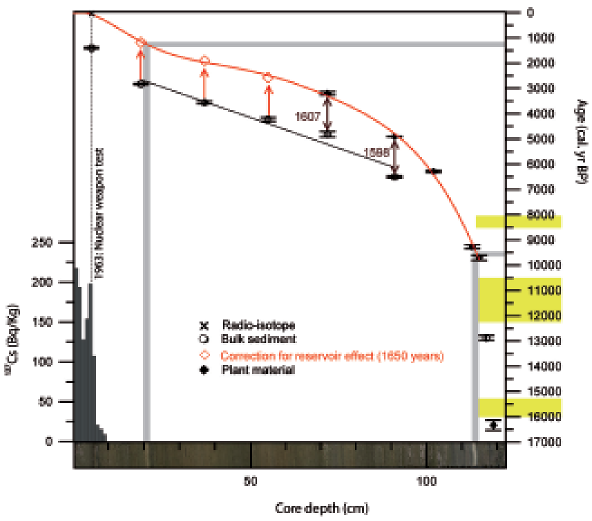

Figure 3. Age model of the sedimentary sequences from Meidsee (modified from Thevenon et al., 2011), using the ^{137}Cs peak (1963), the ages in calendar years bc/ad of macrorests and bulk sediment samples, after the correction for the reservoir age of the sediment of 1650 years (details in Thevenon et al., 2011). The grey-shaded areas highlight the two turbidites mentioned in the text. Post-LGM readvance of mountain glaciers in the northern European Alps are marked by horizontal shading (data from Ivy-Ochs et al., 2004 and 2006).

Pleistocene organic material is discussed further in the results section, while the depth–age curve was generated down to a thin turbidite deposited at 114 cm (~9500 cal. yr BP). The cesium (^{137}Cs) activity profile for the upper part of the core was attributed to the radionuclides global fallout produced by the atmospheric nuclear weapon tests starting in the 1950s with maxima in 1963/1964 (Figure 3; Thevenon et al., 2011).

Late-Pleistocene sediments and the deglaciation (121–113 cm; c. 17,000–9300 cal. yr BP)

It is noteworthy that two of the four radiocarbon dates from the sediment recovered within the first 9 cm of the record yielded pre-Holocene ages, i.e. older than 11.7 cal. kyr BP. One radiocarbon date was measured on terrestrial plant remain (16.3 cal. kyr BP) and one on bulk sediment (12.9 cal. kyr BP) (Figure 3). The presence of Late-Pleistocene OM at those times indicated that the topographic depression was at least episodically filled with water, and testified the absence of a perennial ice cover below 2700 m a.s.l. in the Southern Alps. The radiocarbon dates of organic material deposited about 16, 13, 10, and 9 cal. kyr BP (Figure 3 and details of radiocarbon dates in Thevenon, 2011) therefore evidenced the concomitant deposition and the preservation of organic-rich sediment with carbon isotopic composition typical of aquatic OM (Figures 4 and 5). It is meaningful to note the absence of radiocarbon datable material in between the dated horizons (~15–14, 12–10, and 9–7 cal. kyr BP) that roughly coincide with documented cold climate reversals and Alpine glacier advances (~15, 12–10, and 8 cal. kyr BP; Ivy-Ochs et al., 2006) (Figure 3). Although the Meidsee record does not allow a high-resolution and a detailed analysis of the deglaciation period, the presence of Late-Pleistocene lacustrine sediments at high altitude in the Southwestern Alps pinpoint (1) the absence of perennial ice cover in the alpine catchment that was synchronous with the retreat of the Alpine ice-sheet and with the formation of the perialpine lakes, (2) the absence of a perennial ice cover below 2700 m a.s.l., in between the cold and humid periods of glacier advance documented in the literature (Ivy-Ochs et al., 2004), and (3) the formation of a proglacial lake with in situ production of algal matter from the deglaciation to present. As Meidsee is located on the lateral shoulder of the Turtmann and Rhone Valleys, it is well possible that lacustrine sedimentation already was initiated during

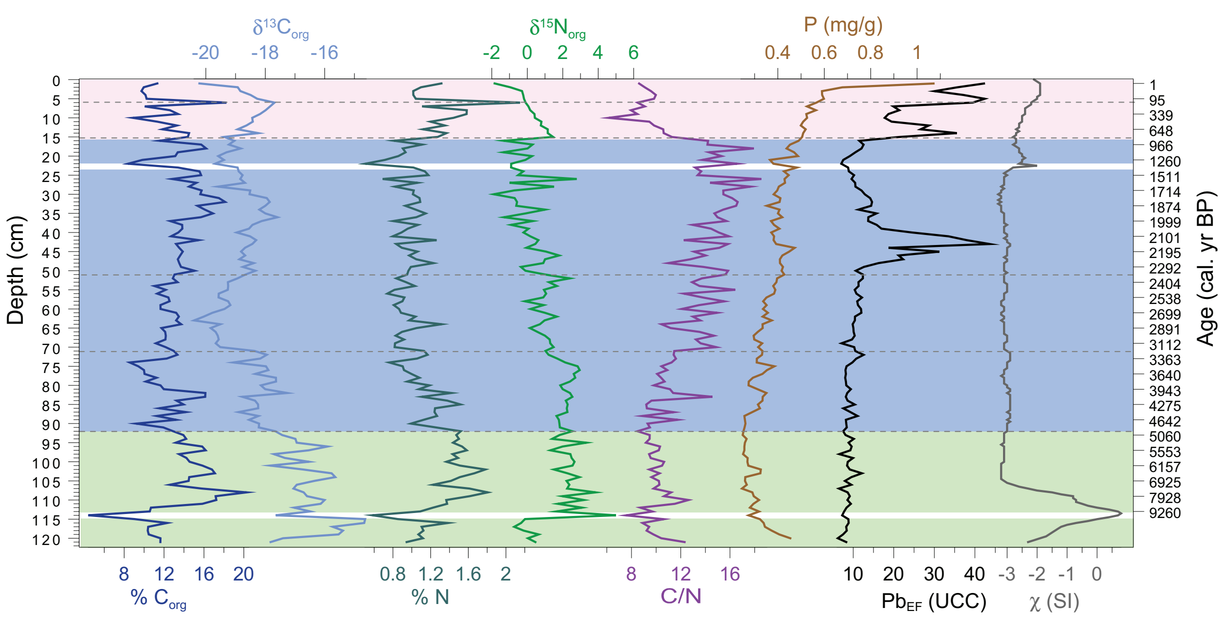

Figure 4. Organic carbon content (C_{org}), $\delta^{13}C_{org}$, nitrogen content (N), $\delta^{15}N_{org}$, C/N ratio, phosphorus (P), enrichment in lead (Pb_{EF}) and magnetic susceptibility (χ). The colored units highlight the main chronostratigraphic units discussed in the text (17–5, 5–0.9, and < 0.8 cal. kyr BP). The two white-shaded areas locate the turbidites mentioned in the text and the dashed lines correspond to the subunits of Figure 5.

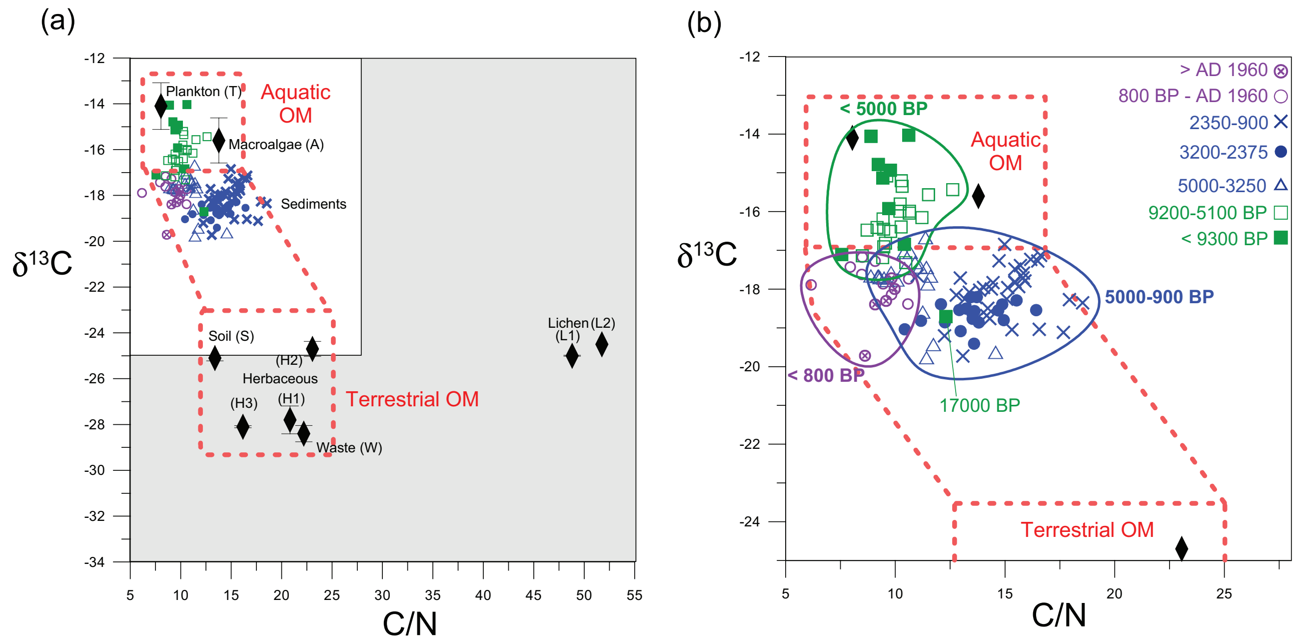

Figure 5. (a) The $\delta^{13}C_{org}$ values versus C/N ratios for Meidsee sediments, with the values for terrestrial and aquatic modern organic matter sources (and SD data from Table 1). (b) Highlight of the white square outlined in (a), with the legend of the chronostratigraphic units discussed in the text and represented on Figure 4 and 5(a).

ongoing glaciation, as the lake may have existed above the elevation of the main-valley glacier.

The basal samples were relatively enriched in by-products of physical weathering (χ), suggesting relatively high erosive inputs (Figure 4). However, the organic parameters clearly excluded a significant contribution of terrestrially derived OM to the sediments at that time, but rather evidenced the strong contribution of aquatic primary productivity (Figure 5). The C_{org} concentration in samples from the bottom of the core (below 113 cm, ~9300 cal. yr BP) was the lowest of the record (Figure 4), indicating a relatively low input of (aquatic) OM into the lake. As shown in Figures 4 and 5, the sediments deposited below the turbidite (before ~9300 cal. yr BP) were characterized by low values of C/N (mean value of 10; n=9), which are typical of fresh algal material contribution (Meyers and Teranes, 2001) and therefore indicated low terrestrial inputs and poor soil development in the catchment. This hypothesis might be confirmed by the concurrent high $\delta^{13}C_{org}$ values that also pointed out the dominant contribution of the algal matter to the OM burden (Meyers and Teranes, 2001). Figure 5 furthermore showed that the $\delta^{13}C_{org}$ fingerprints of the sediment deposited before 5000 cal. yr BP were in good agreement with the isotope composition of modern aquatic samples (mixed plankton and macroalgae, Table 1), demonstrating that (1) the contribution of terrestrial OM remained very low compared with that of lake-derived OM during the first part of the Holocene, and (2) the lacustrine OM which was primarily dominated by aquatic primary productivity remained relatively homogeneous throughout the last deglaciation to the present.

Early Holocene and Holocene climatic optimum (113–93 cm; ~9300–5000 cal. yr BP)

A pronounced decrease in χ following the turbidite layer deposited ~9300 cal. yr BP (Figure 4), indicated decreasing erosive input synchronously with the warmer climate conditions that prevailed in the Southern Alps during the Boreal period (*c*. 9000–8000 cal. yr BP) (McDermott et al., 1999). The concentration of C_{org} and N abruptly rose above the turbidite, possibly resulting from a significant change in lake status (lake-level and water depth). Indeed, SEM observations revealed the presence of pyrite framboids in the sediments deposited above the turbidite (Figure 2i) combined with the development of anoxic bottom waters in the deepest part of the lake. Increasing $\delta^{15}N_{org}$ values combined to decreasing $\delta^{13}C_{org}$ composition during this period could therefore result from the development of anoxic conditions in the water column and enhanced OM input, respectively (Bertrand et al., 2009; Lu et al., 2010). In this horizon, the $\delta^{13}C_{org}$ values and C/N ratios averaged −16‰ and 11, respectively, in agreement with the values observed for modern aquatic OM sources (Figure 5a), excluding a significant terrestrial carbon contribution (Meyers and Teranes, 2001). Roughly similar variations were observed for elemental (C_{org} and N content) and isotopic composition of OM ($\delta^{13}C_{org}$, $\delta^{15}N_{org}$), in association with low C/N ratio. Such results suggested that (1) the aquatic primary productivity has played a dominant role in determining the isotope fractionation of aquatic OM, and (2) micro- and macro-algae were the major contributors to OM in the sediments before 5000 cal. yr BP.

The sediments dated from 8 to 5 kyr cal. BP recorded the lowest erosive inputs (χ on Figure 4) and the highest aquatic OM supply to the lake sediment, as demonstrated by high concentrations of C_{org} and N, a low C/N ratio (~10) typical of modern aquatic OM (Figure 5a). The highest $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ values of OM (Figure 4) characterized a section containing green organic gyttja deposited between ~7.0 and 5.5 kyr cal. BP (105–95 cm core-depth, Figure 3). According to the age model, this section could be attributed to the Holocene Thermal Maximum (HTM) or Atlantic period that has been dated between ~8 and 5 cal. kyr BP in the middle and high latitudes of the Northern Hemisphere, where it was generally associated with the early-Holocene boreal summer insolation maximum that caused the rapid Laurentide ice-sheet retreat (Carlson et al., 2009; Renssen et al., 2009; Seppä et al., 2009).

Mid and late Holocene (93–16 cm; ~5000–800 cal. yr BP)

Chironomid-based reconstructions of July air temperatures from the Swiss and the Austrian Alps revealed a distinct cooling trend from ~4500 until 2500 cal. yr BP (Sub-Boreal period), probably linked to changes in summer and winter insolation (Heiri and Lotter, 2005; Ilyashuk et al., 2011). This period was characterized by a succession of glacier advances and timberline depressions, attributed to the development of cooler and wetter climate (Deline and Orombelli, 2005; Haas et al., 1998). During the second part of the Holocene, Meidsee recorded a smooth but continuous rise in P input (Figure 4) and in C/N ratios (Figure 4), suggesting the relative decline of aquatic OM source with regards to higher inputs of terrestrial OM (Schmidt et al., 2002). The lowest $\delta^{13}C_{org}$ values of the record, between 3200 and 900 cal. yr BP, were therefore certainly influenced by the maxima in terrestrial OM contribution to the lake sediment at those times (Figures 4 and 5). It is however meaningful to note a relative increase in $\delta^{13}C_{org}$ values between *c*. 2200 and 1700 cal. yr BP despite increasing C/N ratios. The enrichment in $\delta^{13}C_{org}$ concomitant with a higher input of C_{org} and OM from terrestrial plants suggests increased lake productivity triggered by the development of a more productive soil layer during favorable climatic conditions (Koinig et al., 2010; Mourier et al., 2010). This interpretation is consistent with the reduction in the size of Alpine glaciers inferred between 2740 and 2500 cal. yr BP (Holzhauser, 1997; Hormes et al., 2001) and with the subsequent amelioration of the climatic conditions during the Roman times in the Western European Alps (Sub-Atlantic period). As demonstrated in Thevenon et al. (2011), a record of anthropogenic lead enrichment from Meidsee highlights the large-scale atmospheric pollution of the Northern Hemisphere due to Greek and Roman mining activities 2000 years ago (Figure 4). However, the organic proxies measured on the same sediment samples clearly exclude a significant human impact in this high-altitude Alpine landscape during the Roman Period (Figure 4).

The last millennium (> 16 cm; ~800 cal. yr BP)

Although P input and soil erosion continued to increase continuously over the last millennium, we observed an abrupt drop in C/N ratios typical of aquatic OM sources (Figures 4 and 5). This shift in OM source around 800 cal. yr BP was the most important change of the last millennia. Moreover, this event strikingly coincided with an increase in the deposition of anthropogenic lead (Figure 4) and with the migration of the Walser people who from the 12th to the 13th centuries spread into several high-alpine valleys of the Southwestern Alps (Pawson and Egli, 2001). A synchronous drop in C/N ratio could therefore indicate an increase in primary production of algae triggered by enhanced nutrient supply linked to human activities (e.g. extended land use). The end of the Walser period 500 years ago (Malacarne et al., 2005) probably linked to climatic deterioration and unfavorable environmental conditions in the Alpine landscape, coincided with a drop in the anthropogenic lead deposition in Meidsee (Figure 4) and with the onset of the ‘Little Ice Age’ (LIA) and Alpine glacier advance (Holzhauser et al., 2005).

Although there was no significant change in the dominant source of aquatic OM during the past few decades, a significant increase in P-input occurs after ~AD 1963 (identified at ~6 cm depth with the maximum ^{137}Cs activity; Figure 2). Surprisingly, the other organic compounds (N and C_{org} contents) do not parallel the increase in P, whereas the $\delta^{13}C_{org}$ values are decreasing. However, the pattern of P-nutrient release to the lake strongly suggests a higher human impact during the last decades, as supported by the abundant animal excrements (Figure 2f) found in the catchment during summer period, as well as by the fish introduction (Figure 2g) and the presence of human wastes into the lake (Figure 2g). These observations excluded a purely paleoclimatic interpretation derived from the uppermost lacustrine sediments of this high-altitude remote Alpine lake, because of enhanced input of terrestrial OM from the watershed.

Conclusion

Meidsee pre-Holocene sediments deposited synchronously with the early formation of Alpine soils and (peri-) Alpine lakes ~17 kyr BP, witness the rapid decay of the perennial ice cover below 2700 m a.s.l. in the Southwestern Alps. Before 5 kyr cal. BP, high $^{13}\delta C$ values (−17 to −16‰) and low C/N ratios (~10) similar to modern aquatic OM fingerprint, indicate that the sedimentary organic matter was primarily constrained by the aquatic primary production. High $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ values were recorded during the Holocene thermal maximum between ~8 and 5 kyr cal. BP, attesting a reduced contribution of terrestrial vegetation. During the second part of the Holocene, decreasing $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ values concomitant with increasing C/N ratio and P input, were likely attributed to the continuous increased contribution of terrestrial organic matter linked to the development of a vegetated landscape. The major environmental change of the Holocene period occurred ~800 years ago, with an abrupt decrease in C/N ratios typical of algal-derived OM from in situ production. However, increasing P-nutrient input and soil erosion synchronously with a strong increase in the deposition of anthropogenic lead, strongly suggest human disturbances by the Walser Alemanic people who extended settlement and important land-use changes at high altitude in the Swiss Southern Alps. During the last decades, human disturbances in the catchment (e.g. cattle grazing and fish introduction) impacted the sedimentary organic matter record. The elemental and isotopic compositions of the high-altitude lake Meidsee therefore demonstrate that climate- and anthropogenic-induced changes in the Alpine landscape primarily influenced the stable isotopes in the lacustrine sedimentary organic matter over the last millennia.

Acknowledgments

We are grateful to Michael Hilbe for the coring campaign on Meidsee, and to Lukas Glur for the opening and logging of the cores at the Limnogeology Laboratory (Geological ETH Zurich).

Funding

This research was financed by a grant from the Swiss National Science Foundation (SNSF Ambizione fellowship).

References

Beniston M (2006) Mountain weather and climate: A general overview and a focus on climatic change in the Alps. *Hydrobiologia* 562: 3–16.

Bertrand S, Sterken M, Vargas-Ramirez L et al. (2009) Bulk organic geochemistry of sediments from Puyehue Lake and its watershed (Chile, 40°S): Implications for paleoenvironmental reconstructions. *Palaeogeography Palaeoclimatology Palaeoecology* 294: 56–71.

Carlson AE, Anslow FS, Obbink EA et al. (2009) Surface-melt driven Laurentide ice-sheet retreat during the early Holocene. *Geophysical Research Letters* 36: L24502.

Deline P and Orombelli G (2005) Glacier fluctuations in the western Alps during the Neoglacial, as indicated by the Miage morainic amphiteatre (Mont Blanc massif, Italy). *Boreas* 34: 456–467.

Eaton DA, Clesceri LS and Greenberg AE (1995) *Standard Methods, 19th Edition for the Examination of Water and Wastewater*. Washington DC: American Public Health Association.

Egli M, Sartori G, Mirabella A et al. (2009) Effect of north and south exposure on organic matter in high Alpine soils. *Geoderma* 149: 124–136.

Favilli F, Egli M, Cherubini P et al. (2008) Comparison of different methods of obtaining a resilient organic matter fraction in Alpine soils. *Geoderma* 145(3–4): 355–369.

Girardclos S, Fiore J, Rachoud-Schneider AM et al. (2005) Petit-Lac (western Lake Geneva) environmental and climate history from deglaciation to present: A synthesis. *Boreas* 34: 417–433.

Haas JN, Richoz I, Tinner W et al. (1998) Synchronous Holocene climatic oscillations recorded on the Swiss Plateau and at timberline in the Alps. *The Holocene* 8: 301–309.

Harwart S, Hagedorn B, Melles M et al. (1999) Lithological and biochemical properties in sediments of Lama Lake as indicators for the late Pleistocene and Holocene ecosystem development of the southern Taymyr Peninsula, Central Siberia. *Boreas* 28: 167–180.

Heiri O and Lotter AF (2005) Holocene and Lateglacial summer temperature reconstruction in the Swiss Alps based on fossil assemblages of aquatic organisms: A review. *Boreas* 34: 506–516.

Holzhauser H (1997) Fluctuations of the Grosser Aletsch Glacier and the Gorner Glacier during the last 3200 years: New results. In: Frenzel B (ed.) *Glacier Fluctuations During the Holocene*. Gustav Fisher Verlag, pp. 35–38.

Holzhauser H, Magny M and Zumbühl HJ (2005) Glacier and lake-level variations in west-central Europe over the last 3500 years. *The Holocene* 15: 789–801.

Hormes A, Müller BU and Schlüchter C (2001) The Alps with little ice: Evidence for eight Holocene phases of reduced glacier extent in the Central Swiss Alps. *The Holocene* 11: 255–265.

Ilyashuk EA, Koinig KA, Heiri O et al. (2011) Holocene temperature variations at a high-altitude site in the Eastern Alps: A chironomid record from Schwarzsee ob Sölden, Austria. *Quaternary Science Reviews* 30(1–2): 176–191.

Ivy-Ochs S, Kerschner H, Kubik PW et al. (2006) Glacier response in the European Alps to Heinrich Event 1 cooling: The Gschnitz stadial. *Journal of Quaternary Science* 21: 115–130.

Ivy-Ochs S, Schäfer J, Kubik PW et al. (2004) Deglaciation timing on the northern Alpine foreland (Switzerland). *Eclogae geologicae Helvetiae* 97: 47–55.

Kelly MA, Buonchristiani J-F and Schlüchter C (2004) A reconstruction of the Last Glacial Maximum ice-surface geometry in the western Swiss Alps and contiguous Alpine regions in Italy and France. *Eclogae geologicae Helvetiae* 97: 57–75.

Kelly MA, Ivy-Ochs S, Kubik PW et al. (2006) Chronology of deglaciation based on ^{10}Be dates of glacial erosional features in the Grimsel Pass region, central Swiss Alps. *Boreas* 35: 634–643.

Koinig KA, Drescher-Schneider R, Hirt A et al. (2010) Soil development as trigger for lake productivity in a high alpine ecosystem. *Geophysical Research Abstracts* 12: EGU2010-13025.

Leng MJ and Marshall JD (2004) Palaeoclimate interpretation of stable isotope data from lake sediment archives. *Quaternary Science Reviews* 23: 811–831.

Lister G (1988) A 15,000 year isotopic record from Lake Zurich of deglaciation and climatic change in Switzerland. *Quaternary Research* 29: 129–141.

Lu Y, Meyers PA, Eadie BJ et al. (2010) Carbon cycling in Lake Erie during cultural eutrophication over the last century inferred from the stable carbon isotope composition of sediments. *Journal of Paleolimnology* **43:** 261–272.

Malacarne E, Danubio ME and Gruppioni G (2005) The effects of geographical and prolonged cultural isolation on the marital behaviour of an Alpine community (Valsesia-Italy, 1618– 1899). *Human Evolution* 20(2–3): 167–179.

McDermott F, Mattey DP and Hawkesworth C (1999) Centennial-scale Holocene climate variability revealed by high-resolution speleothem d18O record from SW Ireland. *Science* 294: 1328–1331.

Meyers PA (1997) Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Organic Geochemistry* 27: 213–250.

Meyers PA and Teranes JL (2001) Sediment organic matter. In: Last WM and Smol JP (eds) *Tracking Environmental Changes Using Lake Sediment, Vol. 2: Physical and Geochemical Methods*. Dordrecht: Kluwer Academic, pp. 239–270.

Mourier B, Poulenard J, Carcaillet C et al. (2010) Soil evolution and subalpine ecosystem changes in the French Alps inferred from geochemical analysis of lacustrine sediments. *Journal of Paleolimnology* 44: 571–587.

Pawson E and Egli H-R (2001) History and discovery of the European and New Zealand Alps. *Mountain Research and Development* 21(4): 350–358.

Renssen H, Seppa H, Heiri O et al. (2009) The spatial and temporal complexity of the Holocene thermal maximum. *Nature Geoscience* 2: 410–413.

Schlüchter C (1988) The deglaciation of the Swiss-Alps: A paleoclimate event with chronological problems. *Bulletin de l'Association française pour l'étude du Quaternaire* 2/3: 141–145.

Schmidt R, Koinig KA, Thompson R et al. (2002) A multi proxy core study of the last 7000 years of climate. *Journal of Paleolimnology* 38: 541–554.

Seppä H, Bjune AE, Telford RJ et al. (2009) Last nine-thousand years of temperature variability in Northern Europe. *Climates of the Past* 5: 523–535.

Talbot MR and Johannessen T (1992) A high resolution palaeoclimatic record for the last 27,500 years in tropical West Africa from the carbon and nitrogen isotopic composition of lacustrine organic matter. *Earth and Planetary Science Letters* 10: 23–37.

Teranes JL and Bernasconi SM (2005) Factors controlling δ^{13}C values of sedimentary carbon in hypertrophic Baldeggersee Switzerland, and implications for interpreting isotope excursions in lake sedimentary records. *Limnology and Oceanography* 50: 914–922.

Thevenon F, Guédron S, Chiaradia M et al. (2011) (Pre-) historic changes in natural and anthropogenic heavy metals deposition inferred from two contrasting Swiss Alpine lakes. *Quaternary Science Reviews* 30(1–2): 224–233.

Xu H, Ai L, Tan L et al. (2006) Stable isotopes in bulk carbonates and organic matter in recent sediments of Lake Qinghai and their climatic implications. *Chemical Geology* 235: 262–275.