Stable oxygen and carbon isotopes of carbonates in lake sediments as a paleoflood proxy

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ABSTRACT

Lake sediments are increasingly explored as reliable paleoflood archives. In addition to established flood proxies including detrital layer thickness, chemical composition, and grain size, we explore stable oxygen and carbon isotope data as paleoflood proxies for lakes in catchments with carbonate bedrock geology. In a case study from Lake Mondsee (Austria), we integrate high-resolution sediment trapping at a proximal and a distal location and stable isotope analyses of varved lake sediments to investigate flood-triggered detrital sediment flux. First, we demonstrate a relation between runoff, detrital sediment flux, and isotope values in the sediment trap record covering the period 2011–2013 CE including 22 events with daily (hourly) peak runoff ranging from 10 (24) m^3 s^{-1} to 79 (110) m^3 s^{-1}. The three- to ten-fold lower flood-triggered detrital sediment deposition in the distal trap is well reflected by attenuated peaks in the stable isotope values of trapped sediments. Next, we show that all nine flood-triggered detrital layers deposited in a sediment record from 1988 to 2013 have elevated isotope values compared with endogenic calcite. In addition, even two runoff events that did not cause the deposition of visible detrital layers are distinguished by higher isotope values. Empirical thresholds in the isotope data allow estimation of magnitudes of the majority of floods, although in some cases flood magnitudes are overestimated because local effects can result in too-high isotope values. Hence we present a proof of concept for stable isotopes as reliable tool for reconstructing flood frequency and, although with some limitations, even for flood magnitudes.

INTRODUCTION

The temporal and spatial limitation of instrumental flood data represents the main limitation for attributing changes in extreme flood occurrence to climate change (IPCC, 2013). Therefore, lake sediments are increasingly explored to extend instrumental flood time series into the past (Gilli et al., 2013; Schillereff et al., 2014; Wilhelm et al., 2018). Paleofloods from lake sediments are reconstructed by detecting flood deposits using microfacies analysis (Mangili et al., 2005; Czymzik et al., 2010; Swierczynski et al., 2013), grain size (Vasskog et al., 2011; Lapointe et al., 2012; Schillereff et al., 2016; Chiverrell et al., 2019), and geophysical and/or geochemical parameters (Thorndycraft et al., 1998; Støren et al., 2010; Wilhelm et al., 2013). However, these approaches require the deposition of clearly discernible flood layers, which are commonly restricted to alpine and arctic regions (Lapointe et al., 2012; Wilhelm et al., 2013) and to major floods exceeding certain magnitudes (Czymzik et al., 2010). Developing additional, sensitive flood proxies can, therefore, provide a basis for deciphering floods of different magnitudes and give access to flood archives from hitherto-unexplored regions (Schillereff et al., 2016). Stable oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotope ratios of bulk carbonates are common proxies in paleolimnological studies, used for reconstructing various climatic and environmental parameters including precipitation, tempera-ture, evaporation, and productivity (Leng and Marshall, 2004). Although even small amounts (5%) of detrital carbonates have been detected in lake carbonate stable isotope records (Mangili et al., 2010), stable isotopes so far have not been applied for paleoflood reconstructions because of the variety of factors controlling stable isotope compositions in bulk carbonate samples (Leng et al., 2010).

Here, we present stable oxygen and carbon isotope compositions of carbonates from sediment cores, sediment traps, and the catchment to discuss their potential for reconstructing both flood frequencies and magnitudes. We have selected Lake Mondsee (in the Upper Austrian region of the Salzkammergut) because the sediments are annually laminated and contain both endogenic calcite and flood-triggered detrital carbonates (Lauterbach et al. 2011; Swierczynski et al., 2012; Kämpf et al., 2014, 2015). The sediment composition resembles that of other alpine lake sediments (Filippi et al., 1998; Czymzik et al., 2010; Wirth et al., 2013), suggesting that the Lake Mondsee sediment record could be representative for other alpine lakes as well.

STUDY SITE AND METHODS

Lake Mondsee is a mesoscale hardwater lake (area ~14 km^2, maximum water depth 68 m) located at the northern fringe of the European Alps (47°48′N, 13°23′E, 481 m above sea level) (Fig. 1). The catchment (~247 km^2) is subdivided into a northern part (~75%), composed of Cretaceous flysch sediments (~50% carbonate rocks) that form relatively smooth hills, and a steep-sloped southern part (25%),
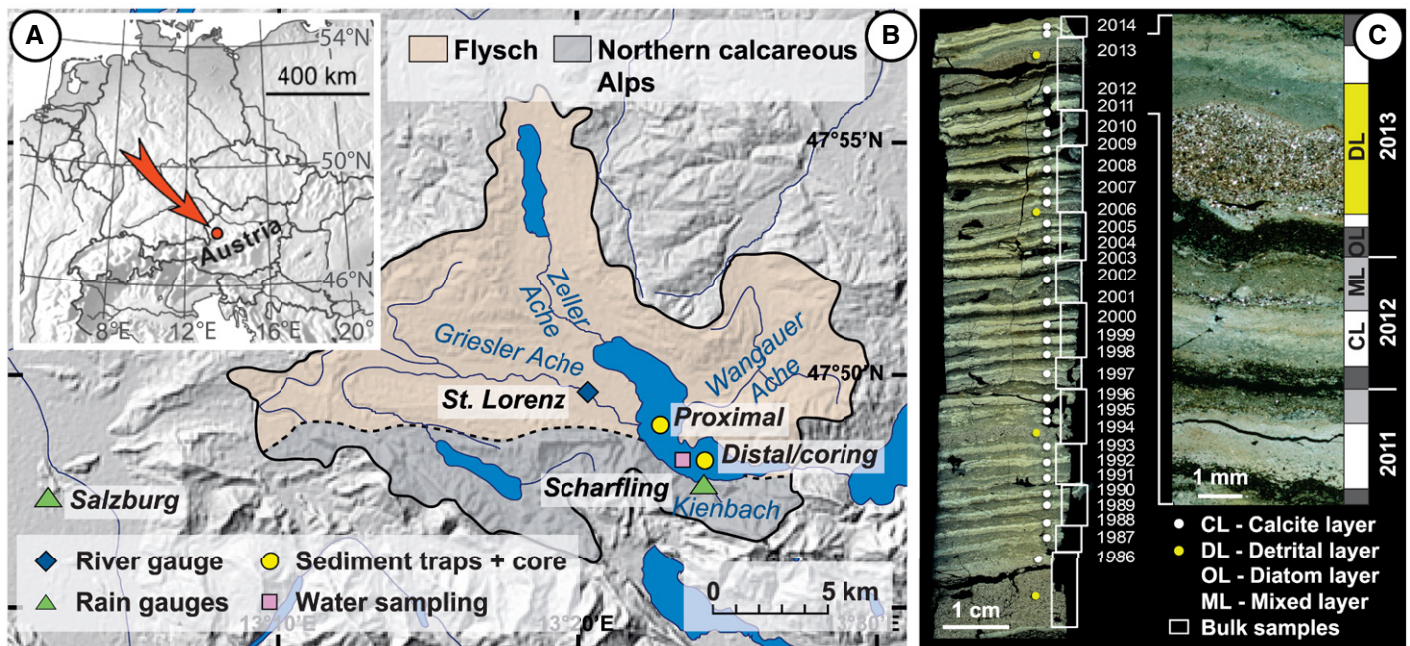
Figure 1. (A) Location map of Lake Mondsee in Austria. **(B)** Catchment area relief, geology, measurement stations, and locations of water sampling, sediment traps, and sediment core. **(C)** Thin-section scans of varved surface sediments, with magnification of interval covered by monitoring data (2011–2013 CE). Indicated are sample intervals of bulk samples (rectangles) and discrete seasonal calcite layers and detrital layers (white and yellow dots, respectively).

which is composed of Jurassic and Triassic limestones and dolomites (Fig. 1). The main tributary Griesler Ache predominantly drains the northern catchment, while the southern catchment is mainly drained by small torrents (Fig. 1).

The sediments were monitored with two moored sediment traps (Fig. 1) at a 3 d time resolution from January 2011 to November 2013 (proximal trap) and from April 2012 to November 2013 (distal trap) (for details, see Kämpf et al., 2015). Stable oxygen and carbon values were determined for all samples. We also measured $\delta^{18}O$ values of lake water samples collected one to three times per month between December 2011 and November 2013 (Appendix DR1 in the GSA Data Repository[1]). Monthly precipitation $\delta^{18}O$ data (Appendix DR1) were provided from a monitoring station in Salzburg by the Austrian Network on Isotopes in Precipitation. The $\delta^{18}O$ and $\delta^{13}C$ values of river-bed sediments were measured from three sub-catchments (Appendix DR2). We

calculated equilibrium $\delta^{18}O$ for calcite precipitation from lake water and compared these values with measured $\delta^{18}O$ from trap samples (Appendix DR3). A varved surface sediment core located near the distal trap location has been investigated by thin-section analyses, allowing sampling of discrete seasonal calcite layers and discrete flood-triggered detrital layers, as well as bulk sediment with a known number of layers included (Fig. 1; Appendix DR4). Griesler Ache runoff was recorded at the St. Lorenz gauge (Fig. 1) by the Hydrographic Survey of Austria.

SEDIMENT TRAP DATA

At both trap sites, carbonates show a distinct seasonal flux pattern with rates of >2 g m^{-2} d^{-1} (2.1–5.4 g m^{-2} d^{-1}, lower–upper quartile) between May and September (summer) and <1 g m^{-2} d^{-1} (0.5–1.0 g m^{-2} d^{-1}) between October and April (winter) (Fig. 2C). Higher summer values reflect biochemical precipitation of calcite, as confirmed by smear slide and scanning electron microscope (SEM) analyses (Fig. DR3-2 in the Data Repository), leading to the formation of calcite varves in Lake Mondsee sediments (Fig. 1). The seasonal pattern is also apparent in the stable O- and C-isotope composition of the trap samples, with relatively high values in winter ($\delta^{18}O$: −6.3‰ to −8.4‰; $\delta^{13}C$: −3.2‰ to −7.1‰) and low values in summer (−8.4‰ to −10.4‰; −5.9‰ to −7.7‰) (Fig. 2). These seasonal variations resemble those in other (peri-)alpine lakes and are controlled by temperature, bioproductivity, and carbonate minerals (Filippi et al., 1998; Teranes et al.,

1999; Teranes and Bernasconi, 2005). The temperature dependence of O isotopes is demonstrated by the comparison of measured $\delta^{18}O$ with the equilibrium composition ($\delta^{18}O_{equil.cc}$ in Fig. 2E) calculated according to Kim and O'Neil (1997) (Appendix DR3). For 62% of all trap samples, the difference between measured and calculated $\delta^{18}O$ ($\Delta_{bulk-equil.cc}$) was <0.5‰, confirming the presence of endogenic calcite. Increased values during both winter (47% of all winter samples) and summer (37%) are related to a higher proportion of detrital carbonates as proven by smear slide and SEM analyses (Fig. DR3-2). In summer, the $\Delta_{bulk-equil.cc}$ values cluster around 14 peaks ranging from +0.5‰ to +5.7‰ (mean: +2.4‰) at the proximal trap site (Fig. 2F). These peak values last for 3–30 d and coincide with increased carbonate flux ranging from 2 to 173 g m^{-2} d^{-1}. For winter samples, eight less-pronounced peaks (+0.5‰ to +2.9‰, mean: +1.4‰) are found because of the generally higher isotope values of these samples, likely due to some contribution of scattered resuspended detrital material from the littoral zone. Distal trap samples from the years 2012 and 2013 exhibit nine peaks of $\Delta_{bulk-equil.cc}$, which all parallel $\Delta_{bulk-equil.cc}$ peaks in the proximal trap. However, the $\Delta_{bulk-equil.cc}$ values are 0.1‰–1.8‰ smaller at the distal site, and no parallel deviations are found at the distal site for five peaks recorded at the proximal site (Fig. 2F). The smaller detrital imprint at the distal site is due to the three- to ten-fold lower sediment load. In general, detrital carbonate flux results in more positive $\delta^{18}O$
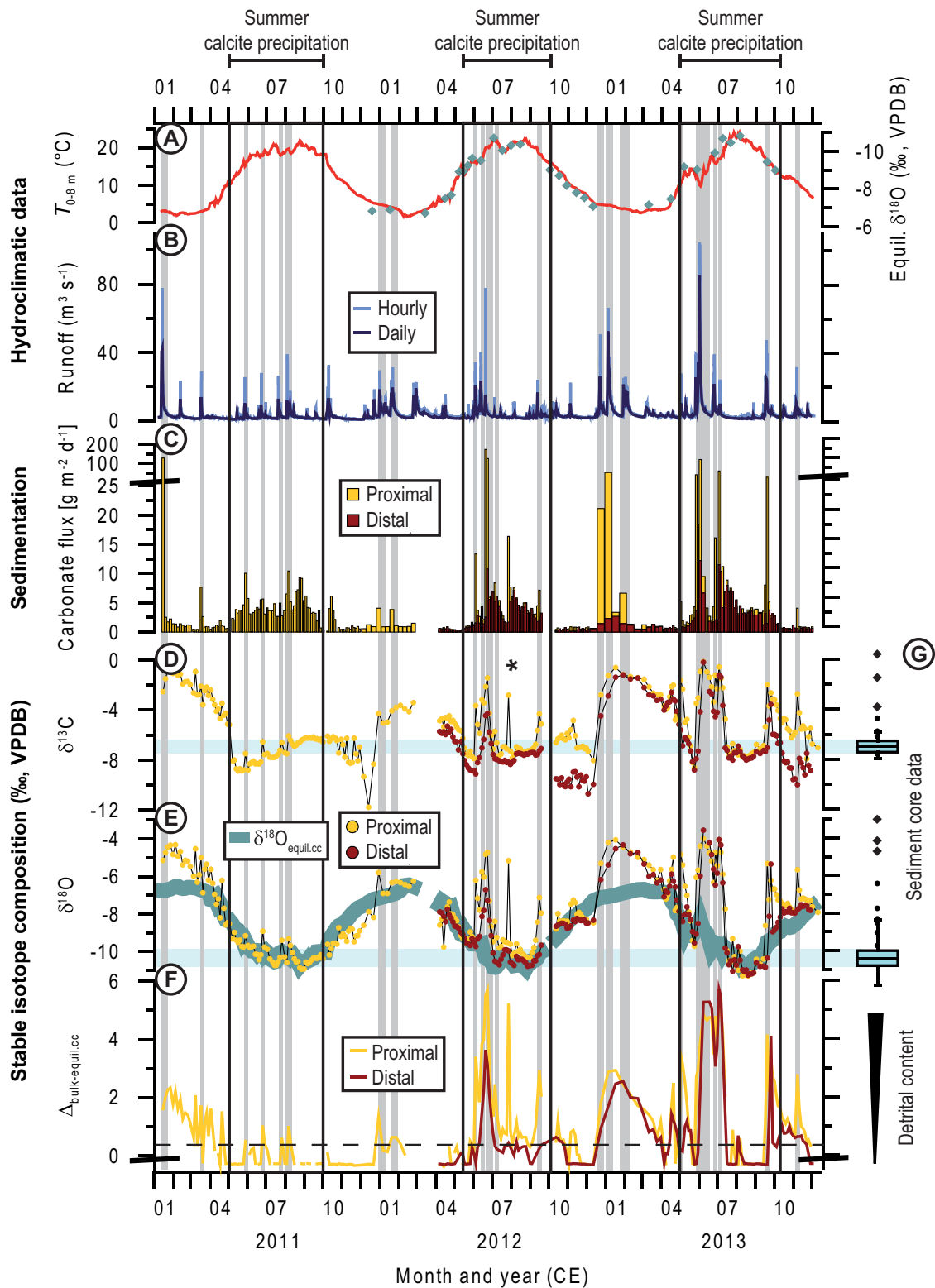
Figure 2. Three years of monitoring data on hydroclimatic variables and trapped sediment at Lake Mondsee (Austria). Gray vertical bars mark flood-triggered peaks in sediment flux and isotopes. (A) Epilimnion (0–8 m depth) water temperature (red line) and calculated equilibrium $\delta^{18}O$ (green diamonds) of endogenic calcite (Appendices DR1 and DR2 [see footnote 1]). (B) River runoff. (C) Carbonate flux. Note change in vertical scale above 25 g m^{-2} d^{-1}. (D) Bulk $\delta^{13}C$ in sediment. Star marks one isotope peak not correlated to runoff due to gap in runoff data. (E) Bulk $\delta^{18}O$ in sediment with calculated endogenic calcite $\delta^{18}O$ ($\delta^{18}O_{equil.cc}$) (Appendix DR2). (F) Differences between measured and calculated endogenic $\delta^{18}O$ ($\Delta_{bulk-equil.cc}$). Horizontal dashed line marks the minimum difference between measured $\delta^{18}O$ and $\delta^{18}O_{equil.cc}$ (0.5 per mil). (G) Bulk $\delta^{13}C$ and $\delta^{18}O$ of calcite layers (box plots, $n = 17$), microscopic detrital layers (dots, $n = 9$), and macroscopic detrital layers (diamonds; $n = 3$). "Proximal" and "distal" indicate proximal and distal sediment traps, respectively (see Fig. 1). VPDB—Vienna Peedee belemnite.

and $\delta^{13}C$ values (Figs. 2D and 2E) reflected in a distinct covariance ($r = 0.9$) of $\delta^{13}C$ and $\delta^{18}O$ (Fig. DR3-3). Covariance is also observed for samples trapped in winter, suggesting redistribution of detrital carbonates from the littoral zone. Sediment trap samples not influenced by detrital carbonate flux show no correlation ($r = -0.3$) between $\delta^{13}C$ and $\delta^{18}O$.

The positive relation between short-term detrital carbonate flux and higher $\delta^{18}O$ and $\delta^{13}C$ values in sediment trap samples is caused by the stable isotope composition of the carbonates in the northern flysch and the southern limestone-dolomite catchments (Appendix DR2). In general, bed-load $\delta^{18}O$ and $\delta^{13}C$ values are 5‰–10‰ higher than those of endogenic calcite, with the

highest value measured for the southern catchment. While the proximal site receives detrital sediments only from the northern catchment, the distal site occasionally receives additional sediment from the southern catchment through runoff from the Kienbach creek, like, e.g., during the large June 2013 flood. This has led to even higher $\delta^{18}O$ values in the distal trap ($\delta^{18}O = -3.5‰$

and $\delta^{13}C = -0.2‰$) than in the proximal trap ($\delta^{18}O = -4.0‰$ and $\delta^{13}C = -0.1‰$).

RECENT SEDIMENT CORE DATA

We measured the stable isotope composition of discrete seasonal calcite layers ($n = 26$), detrital layers ($n = 3$), and bulk sediment samples ($n = 10$) integrating 1–3 yr (0.5–1 cm) in a surface sediment core for the time interval from 1988 to 2013 CE (Fig. 1C; Table DR4 in the Data Repository). Because the $\Delta_{bulk-equil.cc}$ between endogenic and detrital carbonates in sediment cores cannot be calculated directly as for the trap samples, the detrital contribution in stable isotope data was estimated from the maximum difference from previous and following samples, as proposed by Mangili et al. (2010).

The highest isotope values are measured for the three macroscopically visible detrital layers in 1994, 2006, and 2013, with differences from neighboring calcite layers of >5‰ (Fig. 3). Calcite layers from 1991, 1997, 2002, 2005, 2009, and 2010 include detrital layers that can be only detected by thin-section analyses (Appendix DR4) and have >0.5‰ $\delta^{18}O$ deviations (Fig. 3). Calcite layers from 1989, 1993, 1995, and 2012 also have >0.5‰ $\delta^{18}O$ deviations but do not include discrete detrital layers. For the remaining calcite layers without visible detrital layers, $\delta^{18}O$ and $\delta^{13}C$ vary from −11.8‰ to −9.9‰ and from −7.9‰ to −5.7‰, respectively, which mirrors the composition of endogenic calcite in sediment trap samples (Fig. 2G). In comparison to discrete layer samples, the ten bulk sediment samples have a lower variability in their stable isotope composition ($\delta^{18}O = -10.1‰$ to $-8.4‰$ and $\delta^{13}C = -6.5‰$ to $-5.1‰$), as expected because they integrate several layers. Four of five bulk samples that include detrital layers >0.8 mm thickness (1991, 1997, 2002, 2013)

have isotopic differences from neighboring samples of >0.5‰ in $\delta^{18}O$.

As for the sediment trap samples containing detrital carbonates, $\delta^{18}O$-$\delta^{13}C$ covariance is observed for all discrete detrital layers and those calcite layers and bulk samples that contain detrital material (Fig. DR3-3), confirming the proposed impact of detrital catchment material on $\delta^{18}O$-$\delta^{13}C$ covariance in lake sediments (Mangili et al., 2010).

SEDIMENT STABLE ISOTOPE DATA AS PALEOFLOOD PROXY

After proving the detrital imprint on the stable isotope composition of carbonate in the sediment, we compare the isotope data with instrumental flood time series to further test the potential of stable isotopes as paleoflood proxy. For trapped sediments, we observe 22 peaks in the stable isotope compositions in sediments from the proximal site that coincide with elevated runoff of 24 (10) to 110 (79) $m^3 s^{-1}$ hourly (daily) discharge (Fig. 2). At the distal site, only floods exceeding 38 (20) $m^3 s^{-1}$ are recorded, indicating a site-specific sensitivity of stable isotope compositions of carbonates to flood magnitudes in relation to the distance from riverine inflow.

In the sediment core, all nine flood-triggered detrital layers have $\delta^{18}O$ values >0.5‰ higher than their neighboring samples (Fig. 3). Furthermore, two samples (from 1995 and 2012 CE) also have $\delta^{18}O$ values >0.5‰ higher than their neighboring samples, although the floods in these years did not result in the deposition of discrete detrital layers. This indicates that even minor amounts of scattered detrital material are sufficient to be detected in $\delta^{18}O$ values. These results prove that paleofloods can be reliably traced by stable oxygen isotopes in sediments.

We further test the potential of stable oxygen data to reconstruct flood magnitudes following the hypothesis that the amount of detrital sediment that controls the isotopic deviation is related to runoff magnitude (Wilhelm et al., 2013; Wirth et al., 2013). Therefore, we compare $\delta^{18}O$ deviations with hourly discharge data and define two empiric thresholds for $\delta^{18}O$ deviations, >0.5‰ and >2.3‰ (Fig. 4). All floods with a magnitude >65 $m^3 s^{-1}$ in hourly discharge have $\delta^{18}O$ deviations >0.5‰, and four out of five (1991, 1997, 2002, 2013) high-magnitude floods with >90 $m^3 s^{-1}$ hourly discharge have $\delta^{18}O$ deviations >2.3‰. However, there are also low-magnitude floods (2006, 1994) that cross the >2.3‰ threshold, suggesting that there is no simple linear relationship between flood magnitude and isotope data. A likely explanation for $\delta^{18}O$ deviations above the threshold is a contribution of detrital material with particularly high $\delta^{18}O$ values from the southern catchment. Commonly, only the Griesler Ache supplies material from the northern catchment to the lake, but occasionally the Kienbach creek transports additional detrital material from the southern catchment into the lake as observed during the 2013 flood. In such cases, which we assume also for the 1994 and 2006 floods, isotope values are not only controlled by flood magnitude but also reflect the source of detrital material. In bulk sediment samples, four of the five strongest floods on record (1991, 1997, 2002, 2013) are recognized in isotope data. These findings imply that, in contrast to tracing flood occurrence,
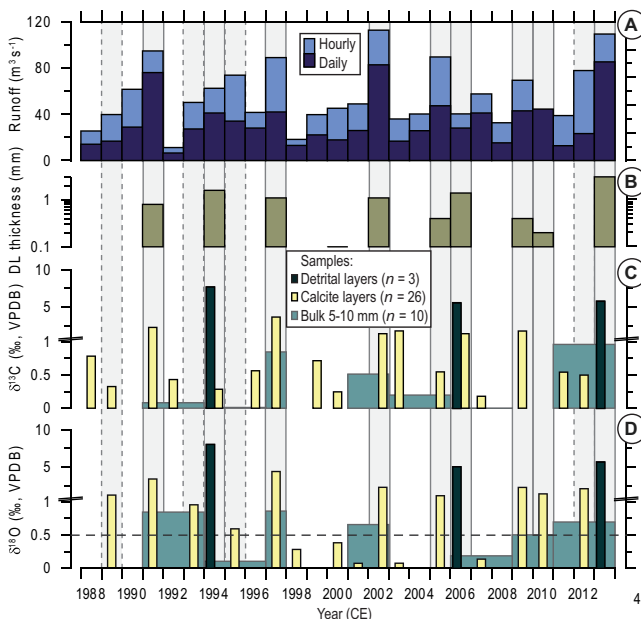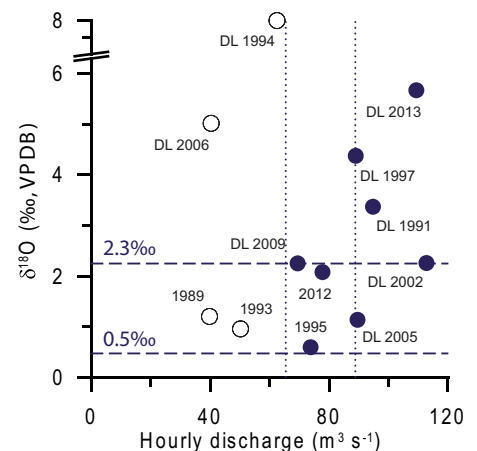
Figure 3. Comparison of hydrological, sedimentological, and stable isotope data from 1988 to 2013 CE at Lake Mondsee (Austria). (A) Seasonal maxima in runoff. (B) Thickness of detrital layers (DL). (C,D) Positive deviations of $\delta^{13}C$ (C) and $\delta^{18}O$ (D) compared to neighboring samples. Note change in vertical scale above 1‰. Horizontal dashed line marks the minimum deviation of $\delta^{18}O$ correlated to a flood-triggered detrital layer (0.5‰). VPDB—Vienna Peedee belemnite. Gray vertical bars with solid borders mark peaks in $\delta^{18}O$ >0.5‰ coinciding with detrital layers and elevated runoff; bars with dashed borders mark isotope deviations without corresponding detrital layers.

Figure 4. Deviations in $\delta^{18}O$ plotted against seasonal maxima in hourly discharge at Lake Mondsee (Austria). Data points are labeled with year of flood event (CE). DL indicates samples comprising a detrital layer. Dashed lines show inferred empirical thresholds in $\delta^{18}O$ deviations for floods >65 $m^3 s^{-1}$ and >90 $m^3 s^{-1}$ (dotted lines). Open circles show samples with larger isotope deviations for floods with hourly discharge below thresholds. One flood event (2010 CE) is not shown due to gap in hourly discharge data set. Note change in vertical scale above 6‰. VPDB—Vienna Peedee belemnite.

flood magnitude reconstruction based on empirical thresholds still has its limitations.

CONCLUSIONS

Through combining sediment monitoring and microfacies analyses of varved sediments from Lake Mondsee, we demonstrate a proof of concept that carbonate O and C isotopes from lake sediments can be reliably applied as paleoflood proxy. Our results prove an unambiguous isotopic imprint of even low-magnitude flood events in the sediment record. Thus stable isotope data are a meaningful complement to classical flood proxies and are applicable to all lakes in carbonaceous catchments with discernible stable isotope signatures of detrital catchment and endogenic lake calcite. Although measurements are straightforward and easy to apply, robust interpretation of lake carbonate stable isotopes require an in-depth knowledge about the depositional processes in the lake and the catchment geology. Provided this information, stable isotopes have a great potential for reconstructing frequencies and, with some limitations, magnitudes of paleofloods.

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