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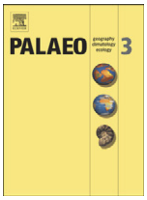

The oxygen and carbon isotopic signatures of biogenic carbonates in Gerzensee, Switzerland, during the rapid warming around 14,685 years BP and the following interstadial

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ABSTRACT

The stable isotope signature of ostracods, molluscs, and charophyte remains from the late glacial section of a shallow core from lake Gerzensee, Switzerland, is analyzed along with the bulk carbonate isotope composition in a multi-proxy study aiming to document the biotic responses to the first strong warming ca. 14.6 ka ago after full glacial conditions. The main goal of our contribution is to understand the climatic significance of the oxygen-isotope variations in and between the different carbonate species and ideally provide a quantitative estimate of the oxygen isotopic composition of meteoric precipitation, which then could be translated to mean temperature estimates. Corrected for the respective vital offsets, the different carbonates show almost identical oxygen-isotope ratios for the time preceding and after the rapid transition from Greenland climate stages GS2 to GI1, indicating low and seasonally constant water temperatures at the sediment–water interface for this period. In the following the difference between cold season and warm-season carbonates increases gradually, pointing to a summer–winter temperature difference of roughly 10 K at the end of GI1. We conclude that this gradual water-temperature increase is independent of climate and is mainly due to sedimentation, shallowing the sediment–water interface, eventually accentuated by a gradual decrease of Gerzensee's water level during GI1. Corrected for the isotope fractionation induced by the long term trend of such water temperature change, the higher resolved δ^{18}O record from the bulk carbonates allows calculation of the presumed oxygen–isotope ratio of former lake water ($\delta^{18}O_L$), which shows striking similarity to the record from Ammersee. Introducing a tentative hydrological correction close to the present day offset between $\delta^{18}O_L$ and the oxygen–isotopes in meteoric precipitation ($\delta^{18}O_P$), we propose a quantitative $\delta^{18}O_P$ and mean air temperature record for the Gerzensee region.

1. Introduction

Bulk-carbonate oxygen–isotope records of lake sediments ($\delta^{18}O_{Cc}$) from Gerzensee in central Europe show typical variations during the last deglaciation that strongly resemble those in the Greenland ice cores (Oeschger et al., 1984; Eicher, 1987; Dansgaard et al., 1989). Major shifts, such as the increase at the transition from the Oldest Dryas to Bølling chronozones and the decrease (increase) at the beginning (end) of the Younger Dryas, show up in almost all European sites examined (Whittington et al., 1996). More detailed records in addition show negative excursions of δ^{18}O within the Allerød and the Preboreal. These isotopic "fingerprints" most probably reflect variations in the isotopic composition of precipitation ($\delta^{18}O_P$) in the course of climatic variations common to both Greenland and central Europe. However, a quantitative assessment of European $\delta^{18}O_P$ from such records is difficult because secondary effects alter the primary $\delta^{18}O_P$-signal during its transport to the lake and incorporation into the carbonates. In the first step, water "carrying" the momentary isotopic information has to enter the lake by recharge, either directly and/or via groundwater exchange, a mechanism that can change with climate and also differs from lake to lake. In the lake itself heavy isotopes are concentrated through evaporation (Gonfiantini, 1986). Also this offset between δ^{18}OP and the isotopic composition of the lake water (δ^{18}OL) is sensitive to climatic change, either through a change in water input (I), evaporation (E), or relative humidity (h) (Gonfiantini, 1986; Gibson et al., 1993). The final fixation of the $\delta^{18}O_L$-signal in carbonate minerals includes fractionation that depends on the water temperature during carbonate formation (~0.23‰/°C, (Friedman and O'Neil, 1977)), as well as additional

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kinetic or physiological offsets [between +1‰ and +2.3%, depending on the type of organism, (von Grafenstein et al., 1999b)].

The fact that consistent features are found in the majority of Late Glacial $\delta^{18}O_{Cc}$ records from European lakes demonstrates that at least part of the $\delta^{18}O_P$-variability was large enough to overprint such secondary effects. However, most of the differences seen between the individual records, as well as most of the smaller amplitude and shorter time interval variability are most likely due to the above-mentioned secondary hydrologic, lacustrine, and biologic effects. Here we investigate the isotope geochemistry of inorganic and various biogenic carbonates from Gerzensee, concentrating on the transition from the Oldest Dryas to Bölling (GS2 to GI1, according to Lowe et al., 2008) with the aim to disentangle the secondary effects to provide a best estimate of $\delta^{18}O_P$, water temperature and air temperature variations. The reaction of the ostracode fauna to climatic or sedimentological changes will be discussed elsewhere (von Grafenstein et al, in prep). The study is part of a multiproxy effort designed to study the biotic responses to the rapid warming at the GS2–GI1 transition, with the stable-isotope record serving as an independent climatic record. Van Raden et al. (2013–in this issue) present a high-resolution record of $\delta^{18}O$ measured on bulk carbonates and correlated to the $\delta^{18}O$ of NGRIP. Under the assumption that the shifts during termination 1a were synchronous on Greenland and in Central Europe this correlation provides the chronology for the isotope- and biostratigraphies at Gerzensee, which is the main aspect of their paper. Here we concentrate on the quantification and the climatic significance of the oxygen–isotope record.

2. Hydrological and limnological settings

Gerzensee is a small headwater lake within a glacially shaped landscape consisting of Miocene clastic marine sediments. The lake has been disconnected from the glacial drainage system since long before the investigated period. Surface input today is from several artificial, canalized streams draining farmland and forest north of the lake. The natural surface outflow through a small creek cut a valley 1.8 m deep into the damming moraine. Formerly the outflow was used for energy production (von Büren, 1935) through a pipe. The modern isotope hydrology of Gerzensee has been monitored within an earlier project (Ruch, 2001), and parts of the data have already been used to evaluate the isotope shifts at the onset and end of the Younger Dryas stadial (von Grafenstein et al., 2000). We refer to the same data set in the present paper.

3. Material and methods

Material used in this study originates from core GEK, taken from the peat surface within a few meters of the present eastern edge of the lake. The core site most probably was covered by water during the entire period of interest, as indicated by the dominance of silty to sandy carbonates in the cores. The transition from GS2 to GI1 (Oldest Dryas to Bölling) is characterized by a decrease of silicate lithics in the coarse fraction (>125 μm). The lithologic changes are described in more detail by Magny, 2013–in this issue.

Stable-isotope measurements were made on bulk carbonate (see van Raden et al., 2013–in this issue, for sample preparation and treatment), on ostracode valves selected for different species and instars, on shells of the bivalve mollusc *Pisidium*, and on charophyte incrustations. Samples used for the separation of specific carbonates were 1 cm thick and taken at 2 cm distance between 414 cm and 390 cm core depth, continuously every centimeter from 390 cm to 380 cm and from 360 cm to 336 cm. Between 380 cm and 360 cm core depth the sample interval and thickness was 0.5 cm. The samples were dried at room temperature and disaggregated by submersion in a 10%-hydrogen peroxide solution for about 2 h, washed through a 125 μm sieve, and rinsed in ethanol before drying. If available, at least 2 valves from adults, 5 to 9 valves of the last instar before adult (A-1), at least 10 valves from A-2, and about 20 from the smallest instars in the sample (A-3 and A-4) of the dominant ostracode species *Pseudocandona marchica* and *Candona candida* were selected for stable-isotope measurements. We also selected single valves of *Pisidium* and a variable amount of clearly identifiable incrustations of *Chara* sp. stems from each sample.

The stable-isotope composition of the fossil material was determined the using automatic CARBO Kiel/MAT 251 CO_2-preparation and mass-spectrometer system in the Leibniz-Laboratory at Kiel University, Germany. Isotope ratios of the shells are given relative to the PDB Standard in the conventional δ-notation. The PDB-standard is represented by the NBS 20 secondary isotope standard, now replaced by NBS 19 (VPDB-scale, (Coplen, 1995)). There is no offset between the scales. The analytical error at Kiel is typically at ±0.05‰ and ±0.08‰ for δ13C and δ18O, respectively.

We use the age model provided and discussed by (van Raden et al., 2013–in this issue).

4. Results

4.1. Oxygen isotopes

The oxygen isotope values of all specific material analyzed (see Fig. 1) follow similar trends but with offsets in the bulk carbonate values close to the "vital offsets" described for those species (von Grafenstein et al., 1999b, 2000). All analyzed taxa show slightly elevated oxygen isotope values around 400 cm, followed by more negative values from 390 cm to 373.5 cm. The major transition to the "Bölling" occurs in all specific records within less than 2 cm from 373.5 cm to 371.5 with mean amplitudes of 2.7‰ . An intermediate maximum is reached at 370 cm, with values 3.2‰ higher than the last pre-Bölling values, and all values decline by approximately 0.5‰ from 370 cm to 362 cm.

Above 362 cm, the oxygen–isotope values of juvenile candonids, *Pisidium*, and charophyte encrustations continue to follow the decreasing trend of the bulk carbonate record, whereas the adult candonids (mainly *Pseudocandona marchica*) continue to exhibit the high values from the early Bölling period. Adult valves also exhibit more sample-to-sample variation and larger differences between multiple measurements from one sample. This certainly in part due to the small number of valves used for each analysis (one to three valves), compared to juveniles (up to 20 valves per analysis), resulting in a less smoothed variability of the ambient water and/or of the water temperature during calcification in this shallow environment. Bulk carbonates, charophytes, and juvenile candonids show distinct negative excursions around 342 cm and at 338 cm. The $\delta^{18}O$ values of adult candonids remain high at the first of the negative excursions but react with a significant drop at the second. For the interval above 332 cm, sample resolution for our study was too low to continue a detailed comparison to the bulk carbonate isotope record. However, the trend to lower oxygen–isotope values shown in the bulk carbonate record are confirmed by the $\delta^{18}O$ values of *Pisidium* record, whereas the $\delta^{18}O$ values of the adult candonids remain high.

4.2. Carbon isotopes

The carbon–isotope records are more or less parallel to each other, decreasing from 414 cm to 362 cm core depth (Fig. 1). The difference between the carbon–isotopes values in bulk carbonate or charophyte remains and *Pisidium* is roughly 3‰ between 420 cm and 373.5 cm and increasing to 4‰ for the period after the big shift in $\delta^{18}O$. The differences between the respective taxa (including the bulk carbonate, which seems to be dominated by charophyte incrustations throughout the core), is certainly mainly due to the specific mineralization processes and differences in the microhabitat (von Grafenstein et al., 2000). Apart from such offsets, the records follow the variations of the carbon–isotope ratios in the dissolved inorganic carbon, with values close to those measured in adult and juvenile candonids. However, the increase in the $\delta^{13}C$ offsets at the onset of the Bölling and the second -order