Journal of Paleolimnology (2005) 34: 93–105
DOI 10.1007/s10933-005-2400-x

Paleolimnological investigations of anthropogenic environmental change in Lake Tanganyika: VII. Carbonate isotope geochemistry as a record of riverine runoff

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Received 10 July 2004; accepted in revised form 15 January 2005

Key words: Carbon isotope ratio, Lake Tanganyika, Mollusk, Ostracode, Oxygen isotope ratio, River discharge, Stable isotope fractionation

Abstract

Evaporation dominates the removal of water from Lake Tanganyika, and therefore the oxygen isotope composition of lake water has become very positive in comparison to the waters entering the lake. The surface water in Lake Tanganyika has remained relatively unchanged over the last 30 years with a seasonal range of +3.2 to +3.5‰ VSMOW. Water from small rivers entering the lake seems to have a $\delta^{18}O$ value between −3.5 and −4.0‰, based on scattered measurements. The two largest catchments emptying into the lake deliver water that has a $\delta^{18}O$ value between these two extremes. This large contrast is the basis of a model presented here that attempts to reconstruct the history of runoff intensity based on the $\delta^{18}O$ of carbonate shells from Lake Tanganyika cores. In order to use biogenic carbonates to monitor changes in the $\delta^{18}O$ of mixing-zone water, however, the oxygen isotope fractionation between water and shell carbonate must be well understood. The relatively invariant environmental conditions of the lake allow us to constrain the fractionation of both oxygen and carbon isotope ratios. Although molluskan aragonitic shell $\delta^{18}O$ values are in agreement with published mineral-water fractionations, ostracode calcite is ~1.2‰ more positive than that of inorganic calcite precipitated under similar conditions. Ostracode shell $\delta^{18}O$ data from two cores from central Lake Tanganyika suggest that runoff decreased in the first half of this millennium and has increased in the last century. This conclusion is poorly constrained, however, and much more work needs to be done on stable isotope variation in both the waters and carbonates of Lake Tanganyika. We also compared the $\delta^{13}C$ of shells against predicted values based solely on the $\delta^{13}C$ of lake water dissolved inorganic carbon (DIC). The ostracode *Mecynocypria opaca* is the only ostracode or mollusk that falls within the predicted range. This suggests that *M. opaca* has potential for reconstructing the carbon isotope ratio of DIC in Lake Tanganyika, and may be a useful tool in the study of the history of the lake's productivity and carbon cycle.

Introduction

One of the greatest human impacts on Lake Tanganyika is the progressive deforestation of the watersheds surrounding the lake (Cohen et al. 1993, 1996). Natural heavily forested watersheds slow the runoff of rain during the rainy season, improve groundwater infiltration, and significantly

moderate the discharge profiles of rivers emptying into Lake Tanganyika. Deforested catchments quickly become heavily eroded and lead to much larger runoff events during the wet season (Cohen et al. 1996, 2005a; Alin et al. 1999; Wells et al. 1999). The oxygen isotope composition of the lake water and regional rainfall/runoff holds great potential as an indicator of changes in runoff intensity because of large differences in the isotope ratios of these waters. If a study could monitor changes in the oxygen isotope composition of lake water near the mouth of a river, at a location within the mixing zone of river and lake water, it should detect changes in the rate of water delivery to the lake and show any modification of the catchment.

Because the $\delta^{18}O$ of mollusk and ostracode shell records the isotopic composition of the water in which they grow, shells can be used to reconstruct the history of the $\delta^{18}O$ of local waters (e.g. Dettman et al. 1995, 1999, 2004). Although temperature also affects the isotopic composition of mollusk shells and ostracode valves, uncertainties introduced by temperature variation are small ($< 1‰$) because of the small seasonal temperature variation in Lake Tanganyika (3–4 °C – Coulter and Spigel 1991). Therefore the geochemistry of shells from a core taken in one of Lake Tanganyika's 'estuaries' (a region where river and lake water are mixed, such as a river delta) should reflect anthropogenic changes in land cover.

This paper will discuss the stable isotope geochemistry of shell material from Lake Tanganyika sediments as a possible indicator of river discharge rates and how oxygen isotope ratios could be used to document human impact on catchments around the lake. We show that the $\delta^{18}O$ of both mollusks and ostracodes in estuary zones of the lake have recorded variation in the oxygen isotope ratio of local water, and that this can be attributed to variation in runoff. After a brief survey of oxygen isotope hydrology in the Lake Tanganyika catchment, the fractionation between shell material and water will be examined based on a small set of measurements. Finally some preliminary data on the affects of river input on stable isotope ratios will be presented and recommendations for the future development of this approach will be made. In addition, we will take a brief look at carbon isotope ratios in Lake Tanganyika shells as potential tools for paleoenvironmental analysis and show that one species of ostracode, *Mecynocypria opaca*, seems to be in carbon isotope equilibrium with DIC in the lake.

Materials and methods

Water samples, cores, and shells were collected from the near shore regions of Burundi and Tanzania at different times between 1985 and 1999 as part of the ongoing research program of A. Cohen and studies of the Lake Tanganyika Biodiversity Project's Special Study on Sedimentation. Localities can be identified on Figure 1 based on the latitude associated with each sample – all latitudes are in decimal format. All samples were collected along the eastern shore of Lake Tanganyika. For detailed descriptions of coring sites, geochronology and core sedimentology of cores LT98-2M and LT98-18M, see Cohen et al. (2005a), McKee et al. (2005) and Palacios-Fest et al. (2005a, b).

Ostracode shells were cleaned of adhering sediment using only distilled water and a fine paintbrush. Because ostracodes from cores LT98-2M and LT98-18M were juveniles and poorly calcified, it was necessary to lump 20 individuals into a single sample. Mollusk shell powders were drilled using a miniaturized dental drill. Powdered samples were heated under vacuum for 1 h prior to analysis, either at 200 °C for aragonites or 360 °C for calcites. Carbonates were analyzed on a Finnigan MAT 251 mass spectrometer paired with a KIEL automated sample preparation device at the University of Michigan Stable Isotope Laboratory. Standard error of results is $\pm 0.08‰$ for $\delta^{18}O$ and $\pm 0.06‰$ for $\delta^{13}C$, based on a replicate analysis of NBS-19, and University of Michigan internal standards. Water $\delta^{18}O$ was measured on a Finnigan Delta-*S* mass spectrometer using an automated CO_2–H_2O equilibration unit at the University of Arizona. Standardization is based on internal standards normalized to VSMOW and VSLAP. Precision is better than $\pm 0.08‰$ for $\delta^{18}O$. All carbonate values are expressed relative to VPDB, water $\delta^{18}O$ values are relative to VSMOW.

Oxygen isotope ratios and Lake Tanganyika waters

Lake Tanganyika is a tropical meromictic lake lying just south of the equator in the East African

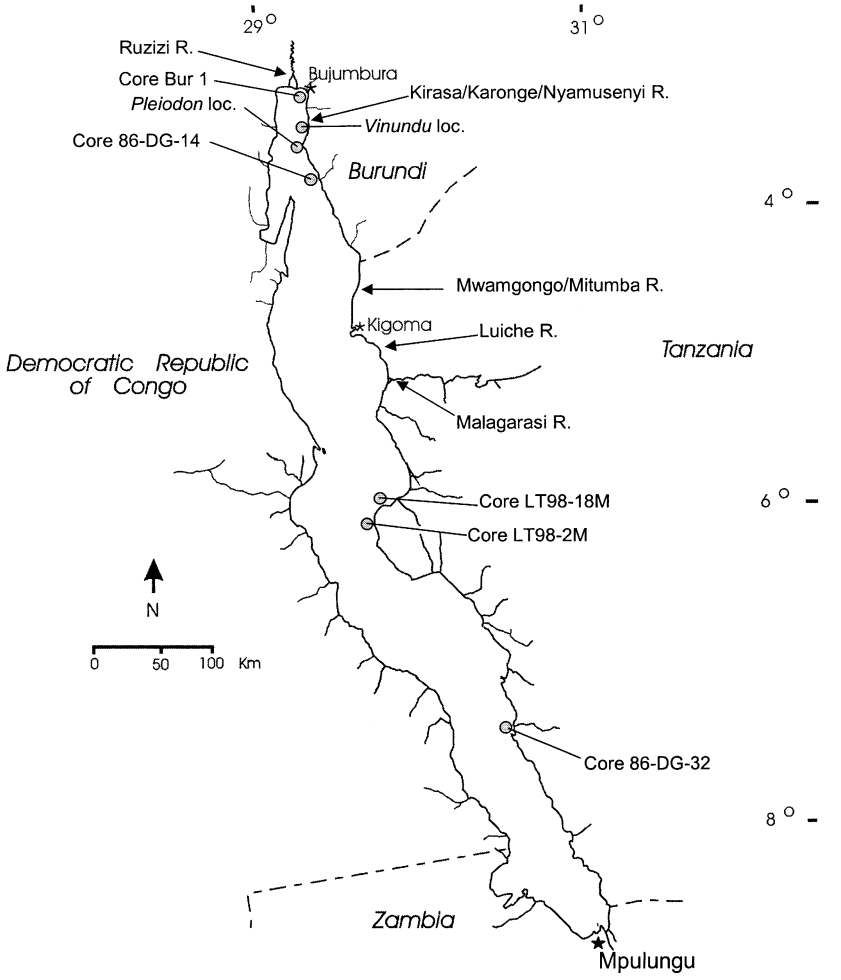

Figure 1. Sample locations.

rift zone (Figure 1). The region receives 900 to 1500 mm rain per year, mostly during a rainy season that lasts from October to April. The lake's surface waters experience a very small seasonal temperature cycle from 24 to 27 °C. Lake Tanganyika is currently an open lake, although the outlet was blocked and the lake was closed for some time prior to 1878 when alluvium in the Lukuga River valley was breached (Cohen et al. 1997). Even now the water balance is dominated by evaporation, i.e., much more of the lake's water loss is through evaporation than through overflow (Craig et al. 1974). Because of this, the oxygen isotope composition of the lake water has become significantly more positive than all inflowing waters. The $\delta^{18}O$ of open lake water ranges from $+3.5‰$ at the surface to $+4.2‰$ below approximately 250 m (Figure 2). The trend to more positive $\delta^{18}O$ values at greater depth is due to times of greater evaporation in the recent past. Some variability is present at the surface where values range from $+3.6$ to $+3.3‰$. Our data show there was little or no change between 1973, when Craig collected water samples, and 1997. Our dry-season (August 1997) average $\delta^{18}O$ value was $+3.6‰$ ($1\sigma = 0.07‰$, $n = 41$). Dry season samples were collected off the Tanzania coast, latitude 4.96° to 4.63° S. Our wet-season (January 1998) average was $+3.2‰$ ($1\sigma = 0.11$, $n = 14$) for samples taken off the Burundi coast (latitude 3.58° to 3.64° S).

Rainfall in this region has a wide range of $\delta^{18}O$ values. Collections just north of Kigoma (Mwamgongo and Mitumba catchments, Latitude

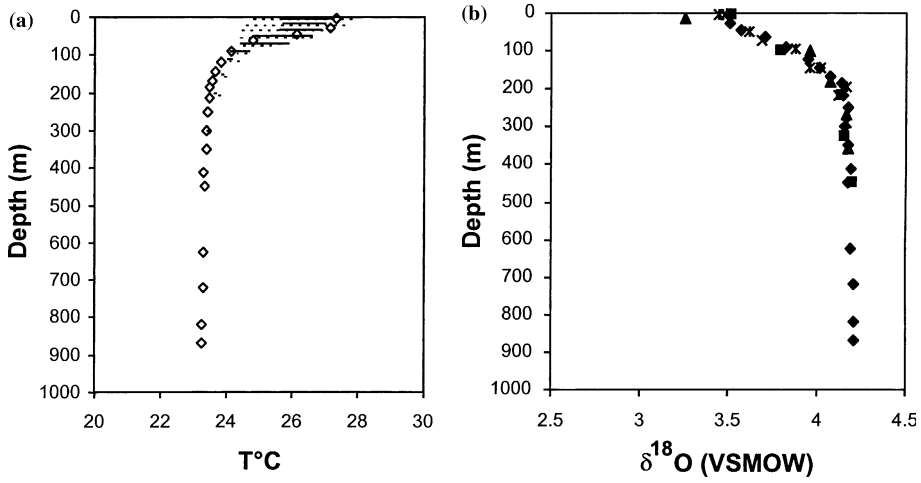

Figure 2. Temperature and $\delta^{18}O$ of Lake Tanganyika waters. (a) Temperature ranges measured by deployed buoys off Kigoma (solid line) and Mpulungu (dashed line) in 1996 (Verberg et al. 1998), and northern basin temperature in February 1973 (diamonds – Craig et al. 1974). (b) Oxygen isotope ratios for offshore Lake Tanganyika water (Craig et al. 1974).

4.6° S) had an average $\delta^{18}O$ of −2.9‰, and ranged from −14.1 to +3.0‰. This rainfall falls on a local meteoric water line defined by:

$$\delta D = 7.50\delta^{18}O + 12.1 \quad (1)$$

(Nkotagu and Mwambo 2000). In 1998, the most positive $\delta^{18}O$ values occurred in September/October and the most negative $\delta^{18}O$ values were in December 1997/January 1998.

Nkotagu and Mwambo (2000) monitored two small rivers intensively in 1997–1998 (see also Nkotagu 2005 for more information on these rivers). The isotopic composition of runoff entering the lake was much less variable than the precipitation during this period. This is because a good deal of the river flow is groundwater, which averages many rainfall events and dilutes isotopic anomalies. River water ranged from −5.3 to −2.3‰ with a standard deviation of 0.6‰ (n = 62). The average $\delta^{18}O$ of these rivers was −3.9 and −3.6‰. The $\delta^{18}O$ of some other rivers have also been measured (Table 1).

Craig et al. (1974) also report river water compositions ranging mostly from −3.8 to −2.8‰. Two large rivers are exceptions to this limited range, the Malagarasi with a $\delta^{18}O$ value of −1.4‰ and the Ruzizi, which carries outflow from Lake Kivu into the northern end of Lake Tanganyika. The Ruzizi ranges from −1.9 to +1.2‰.

The contrast between river waters and lake water is therefore on the order of 6–7‰, with the lake surface ranging from +3.6 to +3.2‰ and rivers ranging from +1.2 to −4.0‰. Smaller groundwater fed streams tend to have values closer to −4.0‰ and rivers with large lakes or wetlands in the catchment tend toward the more positive $\delta^{18}O$ values. The difference between lake water and the local river system becomes the end members of any mixing relationship that tries to quantify runoff into the lake.

Table 1. The oxygen isotope ratio of river waters entering Lake Tanganyika.

River[reference]	Latitude (decimal)	$\delta^{18}O$ (‰ VSMOW)	Date sampled
Kirasa[a]	3.58° S	−3.9	January 1998
Karonge[a]	3.58° S	−3.2	January 1998
Nyamuseni[a]	3.62° S	−3.5	January 1998
Mwamgongo[b]	4.62° S	Avg. −3.6 (n = 33)	Nov. 97–Dec. 98
Mitumba[b]	4.64° S	Avg. −3.9 (n = 29)	Nov. 97–Dec. 98
Luiche[a]	4.96° S	−2.1	August 1997
Luiche[b]	4.96° S	−3.6	April 1998
Malagarasi[b]	5.14° S	−4.2	April 1998
Malagarasi[b]	5.14° S	−0.9	August 1998

Data sources: [a]This study; [b]Nkotagu and Mwambo 2000.

The $\delta^{18}O$ of carbonates in Lake Tanganyika

The oxygen isotope ratios of biogenic carbonates are governed by the $\delta^{18}O$ and temperature of the water in which they grew and many empirical

relationships have been measured for these three variables (e.g. references in Wefer and Berger 1991). While mollusks are often thought to have a very similar oxygen isotope composition to that of inorganic carbonates precipitated in the same environment (Wefer and Berger 1991), a significant offset to more positive values is seen in ostracodes (Holmes and Chivas 2002). In culturing or natural environment studies, all species of ostracode examined have $\delta^{18}O$ values more positive than the $\delta^{18}O$ value predicted for inorganic calcite using the equilibrium fractionation relationship of Friedman and O'Neil (1977). This offset ranges from +2.5 to +0.3‰ with a mean of +1.3‰ (data in Table 2 combined with Holmes and Chivas (2002), Table 3). Note that we do not use the more recent inorganic calcite fractionation relationships of Kim and O'Neil (1997) due to questions of potential disequilibrium in this experiment (Chivas et al. 2002). Therefore, in order to make sure we understand how shells respond to environmental conditions, we will compare the ambient conditions of near-surface lake water with measured $\delta^{18}O$ values (and $\delta^{13}C$ below) of the mollusks and ostracodes collected from sediments in the lake. Unfortunately, we do not have shells from locations in which temperature and the $\delta^{18}O$ of water were measured at the time of growth, nor have we held animals under known conditions, but the relative stability of the lake conditions between 1973 and 1999 suggests that we can use depth profiles of Craig et al. (1974) to constrain the controls on shell $\delta^{18}O$ in the surface waters of Lake Tanganyika.

The upper 50 m of lake water has a seasonal variation of approximately 3 °C (27.4–24.5 °C) and $\delta^{18}O$ ranges from +3.2 to +3.6‰ (Figure 2).

Table 2. Oxygen isotope ratio offset from predicted equilibrium $\delta^{18}O$ value (Friedman and O'Neil 1977) for ostracode calcite – these species supplement offsets tabulated in Holmes and Chivas (2002).

Species	Offset ($\delta^{18}O$ ‰)	Source
Mesocyprideis n.sp. 2B	+1.0	This study (Figure 5)
Mecynocypria opaca	+1.3	This study (Figure 5)
Candonopsis depressa	+1.5	This study (Figure 5)
Candona rawsoni	+1.1 (15 °C)	Xia et al. (1997)
Candona rawsoni	+1.7 (25 °C)	Xia et al. (1997)
Candona subtriangulata	+1.1 (1 °C)	Dettman et al. (1995)

Table 3. Stable isotope data from LT-98 core ostracodes.

CORE LT-98-	cm	species	$\delta^{13}C$ (VPDB)	$\delta^{18}O$ (VPDB)
2M	0.5	*Romecytheridea longior*	−6.1	+2.0
2M	3.5	*Romecytheridea longior*	−5.8	+2.5
2M	6.5	*Romecytheridea longior*	−6.9	+2.5
2M	6.5	*Romecytheridea longior*	−7.0	+2.4
2M	9.5	*Romecytheridea longior*	−7.0	+2.4
2M	12.5	*Romecytheridea longior*	−7.0	+2.4
2M	12.5	*Romecytheridea longior*	−6.0	+2.4
2M	15.5	*Romecytheridea longior*	−6.5	+2.4
2M	18.5	*Romecytheridea longior*	−7.5	+2.3
2M	21.5	*Romecytheridea longior*	−6.4	+2.3
2M	24.5	*Romecytheridea longior*	−6.0	+2.1
18M	0.5	*Romecytheridea longior*	−7.5	+1.7
18M	3.5	*Romecytheridea longior*	−7.6	+1.8
18M	6.5	*Romecytheridea longior*	−7.6	+2.0
18M	9.5	*Romecytheridea longior*	−7.6	+1.7
18M	12.5	*Romecytheridea longior*	−7.8	+1.9
18M	15.5	*Romecytheridea longior*	−6.8	+2.1
18M	18.5	*Romecytheridea longior*	−6.6	+2.2
37M	43.5	*Gomphocythere dowingi*	−4.2	+1.9
37M	43.5	*Mecynocypria opaca*	+1.8	+2.7

At 100 m depth, the seasonal ranges are smaller, temperatures are cooler (24.6–23.9 °C) and the $\delta^{18}O$ value of water is more positive (+3.8 to +4.0‰). Because there is good evidence for mixing of the uppermost 100 m during the dry season (Coulter and Spigel 1991; Verburg et al. 1998), we will use the conditions of the upper 100 m to predict the oxygen isotope ratios of carbonates in equilibrium with these waters. This range of temperatures and $\delta^{18}O$ values combined with the calcite–water fractionation relationship of Friedman and O'Neil (1977) leads to a range of $\delta^{18}O$ values predicted for calcite represented by the rectangle in Figure 3. The predicted range of $\delta^{18}O$ values for aragonite comes from the mollusk aragonite fractionation relationship of Grossman and Ku (1986) as modified by Dettman et al. (1999). The range for predicted calcite $\delta^{18}O$ is +0.7 to +2.1‰ and for aragonite from +1.8 to +3.2‰. Figure 3 shows predicted carbonate $\delta^{18}O$ values for each water $\delta^{18}O$ and temperature from the Craig et al. 1974 report. Note that the upwelling of deeper water will lead to more positive $\delta^{18}O$ values in carbonates.

The oxygen isotope variation in a large bivalve (*Pleiodon spekii*, 5.3 cm by 11.4 cm maximum shell dimensions) collected live on 26 July 1985 along the Burundi shore (Latitude 3.77° S) in 4 m of

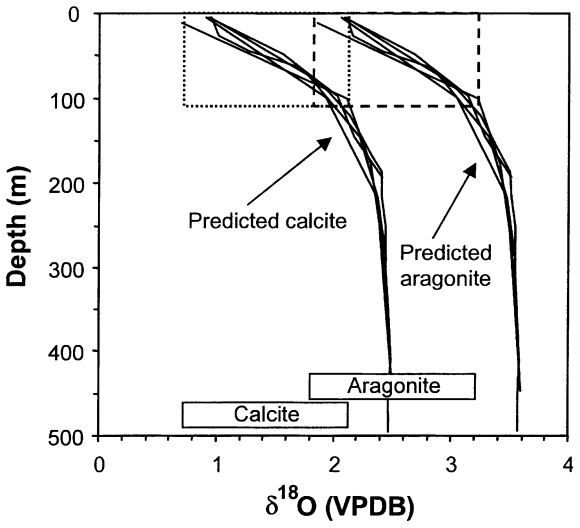

Figure 3. Predicted $\delta^{18}O$ values for inorganic calcite and aragonite at different depths based on temperatures and $\delta^{18}O$ values in Craig et al. (1974). Lines connecting predicted values give a general idea of the possible variation at depths with no data. The rectangles represent the range of $\delta^{18}O$ compositions in the upper 100 m predicted by the fractionations of Friedman and O'Neil (1977) for inorganic calcite and Dettman et al. (1999) for aragonite.

water falls within the range of predicted $\delta^{18}O$ for aragonite in the upper 100 m of water (Figure 4). This shell was analyzed because its locality is away from any significant river input into the lake and the chemistry should represent the typical seasonal cycle for the years 1983–1985. With the exception of one data point, the $\delta^{18}O$ ranges from $+2.0$ to $+2.8‰$. Other modern mollusk specimens, gastropods (*Vinundu* sp.) from the Burundi coastline, also fall within the predicted range. Three samples from a small live *Vinundu westi* gastropod collected in 20 m of water averaged $+2.6‰$, and *Vinundu* sp. fragments from the sediment surface of a core collected at 60 m water depth range from $+3.0$ to $+1.7‰$.

The *Pleiodon* sample shows a muted seasonal cycle with an amplitude of approximately $0.7‰$. This cycle seems to be driven by temperature; if the $\delta^{18}O$ of the water remains constant and the temperature varies by 3 °C, this would create a $0.6‰$ cycle in the shell. The wet season is also the warm season in the lake, and the addition of rainwater to the lake at the time when the surface waters are warmest would lead to more negative $\delta^{18}O$ values in the shell. The other end of the seasonal cycle is the dry and windy season, during which surface waters are cooled through upwelling of cooler water and evaporation. All three of these phenomena (cooling, upwelling, and evaporation) would lead to more positive $\delta^{18}O$ values in the shell. The specimens fall within the range predicted for aragonite, with the exception of a single sample in the *Pleiodon* bivalve. The oxygen isotope cycle in the shell therefore indicates that the bivalve was approximately 2 years old when it was collected. Annual banding is absent in the specimen, apparently because it lived in near-constant conditions throughout its life.

The anomalous $\delta^{18}O$ value in this specimen – a sudden shift to $+1.4‰$ and then a return to more positive $\delta^{18}O$ values, is very suggestive of a runoff event at this location, where near-shore waters are mixed with rain or runoff that is both more negative in oxygen isotope ratio than lake water, and is usually warmer than lake water. This event occurred during the part of the cycle that is moving from maximum $\delta^{18}O$ values (the dry season) to minimum values (the wet season). This probably represents a large rain event during the beginning of the rainy season in 1983. This anomalous sample was replicated to rule-out mass spectrometer errors. Similar results for tropical lacustrine mollusks have been shown by Leng et al. (1999).

We have not measured live-collected ostracode shells from the lake, but published data on ostracodes from cores also suggest that oxygen isotope ratios in ostracode valves can respond strongly to runoff events. In order to quantify runoff events based on the isotopic composition of ostracode valves, we must understand the oxygen isotope fractionation between shell and water. Offsets from the 'equilibrium' calcite $\delta^{18}O$ value (calculated using fractionation of Friedman and O'Neil 1977) seem to vary by species, and each species may need to be calibrated (Holmes and Chivas 2002). Unfortunately, there is no calibration data for the species used in this study, *Romecytheridea longior*, as we have not collected live specimens from Lake Tanganyika. Core data suggest that, in general, the offset for Lake Tanganyika ostracodes is not significantly different that the average measured offset of $1.3‰$. The offset between the 'equilibrium' $\delta^{18}O$ value of calcite and the $\delta^{18}O$ measured for three species of ostracode can be approximated using data from Lake Tanganyika cores in Wells et al. (1999). Figure 5 compares the

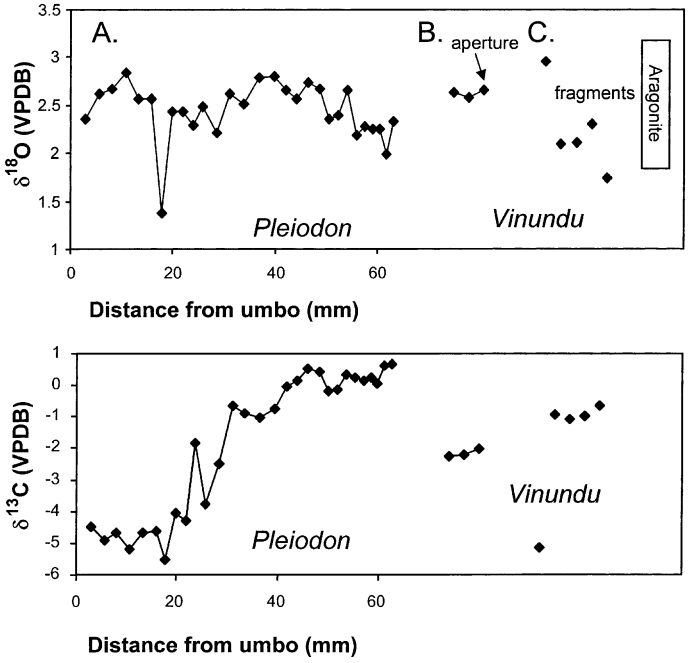

Figure 4. Aragonite shell samples from northern Lake Tanganyika: $\delta^{18}O$ (top) and $\delta^{13}C$ (bottom). (a) Samples were drilled from a cross-section of a live collected *Pleiodon spekii* specimen (collected 26 July 1985 in 4 m water at latitude 3.77° S). (b) Three samples from a single *Vinundu westi* gastropod shell (20 m water depth, latitude 3.64° S). (c) *Vinundu* sp. shell fragments from the core top of 86-DG 14 (Wells et al. 1999). Rectangle (aragonite) shows range of predicted $\delta^{18}O$ values from Figure 3.

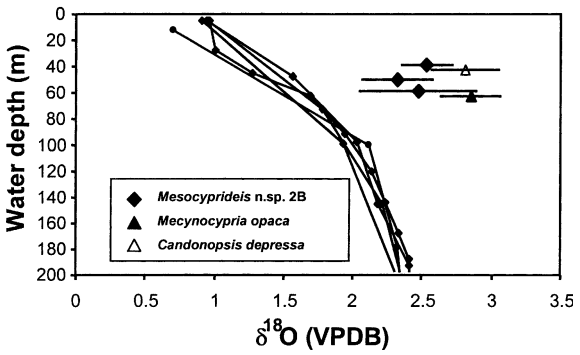

Figure 5. Mean ± 1 standard deviation $\delta^{18}O$ values (horizontal lines) for ostracodes from previously published Lake Tanganyika cores (excluding outliers that may indicate runoff events) plotted at the depth of the core site (Cores 86-DG-32 at 40 m, BUR-1 at 50 m, 86-DG-14 at 60 m; Wells et al. 1999). Two species from cores 86-DG-32 and 86-DG-14 are shown slightly offset from each other for clarity. Lines connecting predicted calcite $\delta^{18}O$ values from Figure 3 are also shown. The average offset from predicted $\delta^{18}O$ values are summarized in Table 2 (see text).

mean ostracode $\delta^{18}O$ from these cores to the predicted calcite $\delta^{18}O$ value based on the measured water conditions in Craig et al. (1974). These cores are thought to span the last 200–400 years (Wells et al. 1999), an interval in which the $\delta^{18}O$ of Lake Tanganyika water and lake levels remained relatively constant (Cohen et al. 1997). Ostracode $\delta^{18}O$ values are plotted against the depth at which the cores were collected. Table 2 summarizes the offset for *Mesocyprideis* n.sp. 2B, *Mecynocypria opaca*, and *Candonopsis depressa* from Lake Tanganyika, as well as two *Candona* species from the literature which were not included in the Holmes and Chivas (2002).

The oxygen isotope record of core 86-DG-14 contains two significant excursions to more negative values (Figure 6). These anomalously negative values also suggest runoff events at the core location. A significant decrease in ostracode diversity and increase in abundance was noted in the upper 7 cm of the core and, although there are a number of possible causes, deforestation and human modification of the Dama River catchment is one suggested reason (Wells et al. 1999). Oxygen isotope ratios nearing 0‰ at the core top also support the possibility that runoff has increased significantly as the catchment was heavily deforested in the 20th century. If this is the case, however, the anomalously negative values at 65 cm core depth

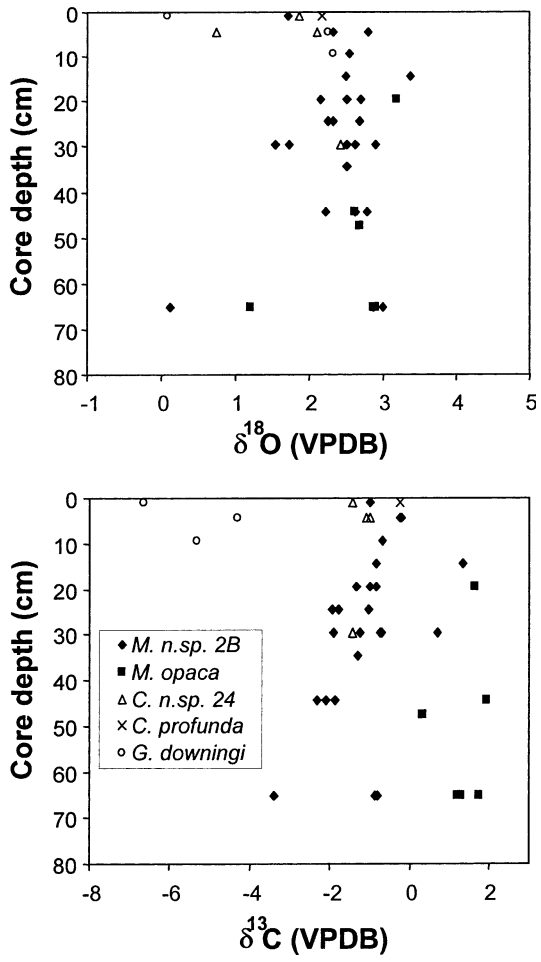

Figure 6. Oxygen and carbon isotope ratios for ostracode shells from core 86-DG-14 (Wells et al. 1999). Each measurement is of a single valve. Species names are listed in caption to Figure 8.

must be attributed to some other reason, as it is thought to pre-date the major deforestation in this area (Wells et al. 1999). Note that the variability of $\delta^{18}O$ values at 1 cm and at 65 cm depth is much greater than elsewhere in the core. This shows that the runoff events are short-term departures from normal conditions in the lake. The oxygen isotope ratio of a single ostracode valve records a very brief period of the environmental conditions in the lake because of the rapid calcification of ostracode shell (hours to days for complete calcification). The analysis of single valves (as in Figure 6) will therefore record the range of conditions as the local environment undergoes short-term changes. This is the most likely explanation for the greater range of $\delta^{18}O$ values measured at 1 and 65 cm.

The $\delta^{18}O$ values close to 0‰ are not possible under the temperature and $\delta^{18}O$ conditions of modern lake water. These oxygen isotope anomalies must record significant runoff events. The stable isotope record reflects change in the isotopic composition of water at one location. Changes in the isotopic composition of the lake water itself can only happen on very slow time scales, thousands of years, due to the long residence time of water in the lake (Craig et al. 1974; Cohen et al. 1997). Therefore short-term or transient changes in shell $\delta^{18}O$ most likely reflect variation in the rate of runoff at one location. Whether these changes in runoff are due to deforestation or to variation in rainfall patterns cannot be discerned solely from stable isotope records. However, stable isotope records may allow us to quantify and establish a history for areas known to have undergone deforestation in the recent past.

Quantifying changes in runoff

Ostracode samples were analyzed from two of the LTBP suite of cores (Table 3): LT-98-2M (latitude 6.17° S, 110 m water depth) and LT-98-18M (latitude 5.98° S, 75 m water depth). We focused on one species of ostracode, *Romecytheridea longior* in this analysis. This species occupies a wide range of habitats in the lake (Palacios-Fest et al. 2005b), is most often found in near-shore muddy environments, and is most likely a good monitor of variation in the isotopic composition of water in the delta caused by changes in runoff into the lake. The oxygen isotope composition of *R. longior* from Core LT-98-2M ranges from +2.0 to +2.5‰ (Figure 7). In core LT-98-18M valves of the same species range in $\delta^{18}O$ from +1.7 to +2.2‰. Because the seasonal cycle in temperature is small in Lake Tanganyika surface waters and because we were forced to use 20 individuals for each sample (probably mixing shells from different seasons) we assume here that the $\delta^{18}O$ of an ostracode sample is primarily controlled by the $\delta^{18}O$ of local lake water. Thus, changes in the $\delta^{18}O$ of ostracode carbonate in a core should directly reflect changes in the $\delta^{18}O$ of the water in which the animals grew.

In order to quantify changes in riverine input at one location using oxygen isotope ratios, the end member $\delta^{18}O$ values of lake and river waters are needed. We do not have river $\delta^{18}O$ data on the two

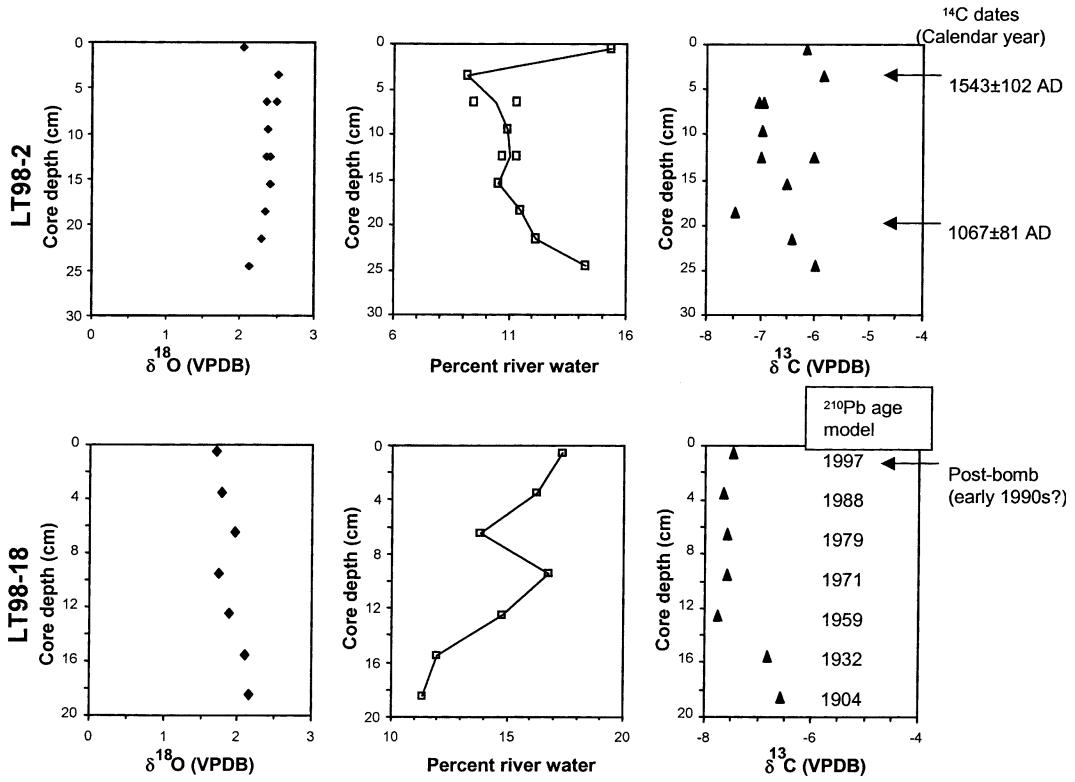

Figure 7. Oxygen and carbon isotope ratios of the ostracode *Romecytheridea longior* from core LT98-2 (top) and LT98-18 (bottom). Each sample is made up of 20 valves. See text for calculation of percent river water. Discussions of core chronology and inferred environmental history can be found in McKee et al. (2005), Cohen et al. (2005b) and Palacios-Fest (2005a, b).

rivers associated with core LT-98-2M (the Lubulungu) or core LT-98-18M (the Kabesi). As shown above, the $\delta^{18}O$ of river water is quite variable, but for rivers in moderate to small catchments, which are appropriate for this study, the average $\delta^{18}O$ is approximately $-3.7‰$ (the mean of data from Table 1, excluding the Malagarasi River). Lake water at depths of 110 and 75 m ranges from $+3.7$ to $+3.9‰$. A linear mixing relationship between the two end members (-3.7 and $+3.8$) can be used to estimate changes in runoff percent at a point on a delta. An equation that relates a change in shell $\delta^{18}O$ (caused by an increase or decrease in the proportion of river water) to the proportion of river water at a location would be of this form:

$$f = \frac{\delta^{18}O_{\mathrm{LTshell}} - \delta^{18}\mathrm{O}_{\mathrm{shell}}}{\delta^{18}\mathrm{O}_{\mathrm{LTwater}} - \delta^{18}\mathrm{O}_{\mathrm{Riverwater}}} \qquad (2)$$

where f is the decimal fraction of river water at the location, $\delta^{18}\mathrm{O}_{\mathrm{LTshell}}$ is the expected value for shell grown in pure lake water, $\delta^{18}\mathrm{O}_{\mathrm{shell}}$ is the measured value of a shell, $\delta^{18}\mathrm{O}_{\mathrm{LTwater}}$ is the ratio of pure lake water, and $\delta^{18}\mathrm{O}_{\mathrm{Riverwater}}$ is the value of the local river water. In the absence of detailed sampling of the waters involved at these two core locations, we will use general estimates for the lake. The denominator of Equation (2) is therefore $+3.8 - (-3.7)$ or $7.5‰$. Based on these end-members, a $1‰$ change in shell $\delta^{18}O$ represents a 0.13 change in the proportion of river water.

To use Equation (2), the $\delta^{18}O$ of shell carbonate grown in pure lake water is needed. The 'equilibrium' $\delta^{18}O$ values for inorganic calcite can be taken from Figure 5; at 110 m the expected $\delta^{18}O$ is $2.0‰$ and at 75 m the average $\delta^{18}O$ value predicted is $1.8‰$. Ostracode calcite is offset to more positive values from this equilibrium calcite $\delta^{18}O$ value, however the species used in this study has not been calibrated. Calibration studies have suggested a range of 0.3 to $2.5‰$ (Holmes and Chivas 2002) and offsets observed for three species in Lake Tanganyika range from $+0.9$ to $+1.5‰$ (Figure 5).

For purposes of discussion here, we will adopt an average value of $+1.2‰$. When this offset is added to the predicted calcite $\delta^{18}O$ value listed above, the expected ostracode shell $\delta^{18}O$ value becomes $+3.2‰$ for core LT98-2 and $+3.0‰$ for core LT98-18 for ostracode shells growing in pure lake water.

Core LT-98-2M, from the Lubulungu Delta, shows a trend in $\delta^{18}O$ toward more positive values higher in the core, and shell $\delta^{18}O$ values are never as positive as that expected for pure lake waters (Figure 7). This implies that runoff percentages decreased at this location over the first half of this millennium. We can model the percentage river water at the core location using Equation (2) to get the percentage river water plotted in Figure 7. The model suggests that the core location has seen a decreasing influence of river water throughout the interval from which we have isotope data. The uppermost sample of the core, falling sometime within the last 500 years, indicates a return to a greater amount of runoff, similar to that of the earliest sample. The percentage of river water decreased from 14% to approximately 9%, with a final increase to 15%.

Core LT-98-18M, from the Kabesi Delta, has a trend toward more negative values toward the top of the core (Figure 7). This probably reflects an increase in runoff amount over the last century at the core location. The model suggests that the proportion of river water (and by inference runoff rates) have increased significantly during the 20th century, from 11 to 17% river water at the core location.

This treatment of the core materials assumes that these ostracodes lived at the core collection depths. If these shells were transported from shallower water, the lake water end member of the mixing relationship would change significantly. In shallower waters both $\delta^{18}O_{LTwater}$ and $\delta^{18}O_{LTshell}$ are more negative, effectively reducing the amount of runoff for any of the $\delta^{18}O$ values reported in Figure 7. For example if ostracodes from Core LT-98-2 were transported from 40 m of water the $\delta^{18}O_{LTshell}$ is $+2.5‰$, identical to the most positive $\delta^{18}O$ values from the core. From this, the river water percentage is 0%, and all river percentages are reduced proportionally. The issue of transport of *R. longior* in these cores is still problematic, with taphonomic indicators (intact valves, no abrasion) suggesting little or no transport, but preferred habitat and the low abundance of adults suggesting displacement, see discussion in Palacios-Fest et al. (2005b).

Clearly this model only offers rough estimates of the mixing of river water with lake water, and to use it to quantify discharge and runoff without more study of the stable isotope systematics in Lake Tanganyika is prone to large uncertainties. Yet, these two small pilot studies agree well with the inferred history of the catchments (Cohen et al. 2005b; Palacios-Fest et al. 2005a, b), and in the absence of any historical record of rainfall and runoff such stable isotope techniques may prove useful in constraining past records of rainfall and human impact in Lake Tanganyika. There is a clear need for a systematic survey of stable isotope ratios of lake water with particular attention to variation in time, with depth and with location in the lake. Also variation in the isotopic composition and volume of river discharge needs to be quantified. Finally, a better understanding of the fractionation of oxygen isotope ratios in various taxa of ostracode is needed before this model is widely applied in Lake Tanganyika and elsewhere.

Stable carbon isotope ratios in shells

The interpretation of carbon isotope ratios in biogenic carbonates is problematic because many factors contribute to the final isotopic composition of a mollusk or ostracode shell. Dissolved inorganic carbon (DIC) in the ambient water clearly plays a large part in the final $\delta^{13}C$ of shell material, but many studies have suggested that metabolic carbon and microenvironmental variation in $\delta^{13}C$ values can play a major role (e.g., Dillaman and Ford 1982; Tanaka et al. 1986; Dettman et al. 1995, 1999; Von Grafenstein et al. 1999; Holmes and Chivas 2002; McConnaughey 2003). The carbon isotope composition of DIC in Lake Tanganyika decreases in the upper 100 m from approximately $1.5‰$ at the surface to $0.3‰$ at 100 m depth (Craig et al. 1974). We will predict the $\delta^{13}C$ shell calcite and aragonite based on the carbon isotope fractionation study of Romanek et al. (1992). That study concluded that the offset between bicarbonate DIC and calcite is $1.0 \pm 0.2‰$, and the offset for aragonite is $2.7 \pm 0.6‰$. They concluded that these differences

are independent of temperature. The pH of Lake Tanganyika water is 8.8–9.2 (Craig et al. 1974) and DIC is almost entirely bicarbonate. These offsets are used in Figure 8 to define fields that represent the equilibrium fractionation between calcite and aragonite and the DIC of the upper 100 m of water in Lake Tanganyika.

Shells used in this study are plotted in Figure 8 to identify species that may be useful for future studies of the carbon cycle and the stable isotope history of DIC in Lake Tanganyika waters. Only one species of ostracode falls within the range predicted for carbonate in carbon isotope equilibrium with DIC, *Mecynocypria opaca*. This species may therefore be useful in future work on the carbon cycle and productivity in Lake Tanganyika. Other species of ostracode and all mollusks are significantly more negative than that predicted by inorganic carbonate fractionations. Many species of ostracodes are infaunal or epifaunal and there may be a significant difference between the $\delta^{13}C$ of DIC in the microenvironment they inhabit (pore water or the sediment–water interface) and that of open lake water. Differences in pH of sediment microenvironments may also affect the relationship of open lake water DIC and shell $\delta^{13}C$. Microhabitat data are not available for most of the ostracodes of Lake Tanganyika, but the close match of the carbon isotope chemistry of *Mecynocypria opaca* and open water DIC suggests that this species prefers habitats removed from the sediment–water interface. We have collected *M. opaca* crawling on rocks and other hard substrates, well above the sediment surface. In addition, many invertebrates incorporate metabolic (food) carbon into their shells, as seems to be the case with freshwater bivalves (Dettman et al. 1999). This leads to shell $\delta^{13}C$ values that are more negative than a shell derived solely from DIC. This is the pattern we see in all mollusks and most ostracode taxa examined in this study.

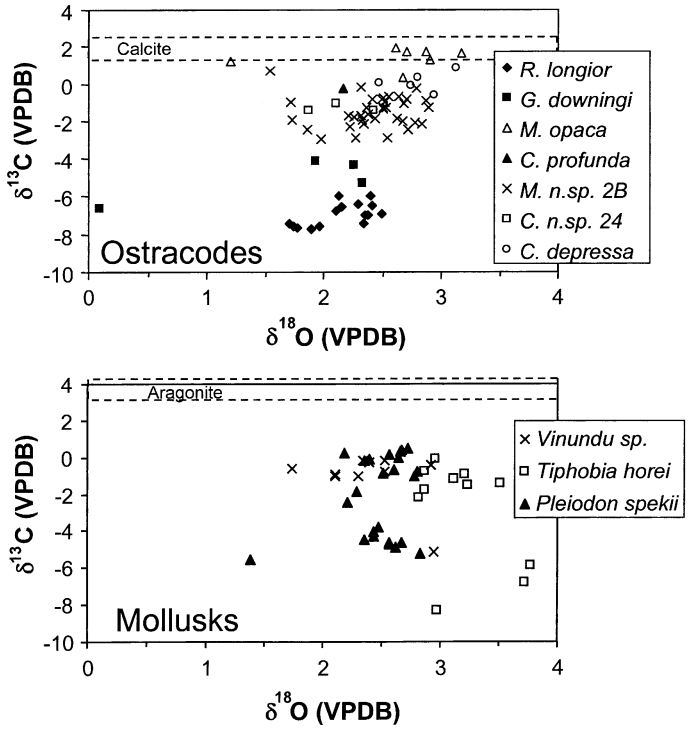

Figure 8. Oxygen and carbon isotope ratios for all ostracode and mollusk shell specimens reported in this paper and in Wells et al. (1999). Ostracode species names are: *Romecytheridea longior, Gomphocythere downingi, Mecynocypria opaca, Cyprideis profunda, Mesocyprideis* n.sp. 2B, *Cyprideis* n.sp. 24, *Candonopsis depressa* (synonomies for species previously published under different names from Alin and Cohen (2003)). The range of predicted equilibrium $\delta^{13}C$ values is derived from data in Craig et al. (1974) and the fractionations of Romanek et al. (1992).

Conclusions

The oxygen isotope ratio of carbonates from Lake Tanganyika cores can be used to reconstruct the history of runoff into the lake because of the large contrast in the typical $\delta^{18}O$ values of inflowing river/rain water and that of lake water. Carbonates from cores have recorded changes in the $\delta^{18}O$ of lake water over long time scales and these records can be used to reconstruct changes in the mixture of river water and lake water near the mouth of a river. Changes in this proportion may reflect changes in rainfall patterns or modification of the catchment by humans. Although the small temperature cycle in lake water and the use of multiple valves help remove uncertainties introduced by seasonal changes in temperature, this work can only model changes until more is known about the variation in the $\delta^{18}O$ of water and shell in Lake Tanganyika.

Acknowledgements

We thank the Lake Tanganyika Biodiversity Project (LTBP) for financial support of this project. Logistical support was generously given by A. Menz and G. Patterson of the LTBP, the crew of the R/V Tanganyika Explorer, the Tanzanian Fisheries Research Institute (TAFIRI), and the Tanzanian Council for Scientific Research (COSTECH). We also thank Ellinor Michel for the *Vinundu* gastropod sample, and both Catherine O'Reilly and Simone Alin for assistance in the field. This is contribution #170 of the International Decade of East African Lakes (IDEAL).

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