Biogeosciences Discuss., 3, 1453–1471, 2006
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Mn seasonal upwellings recorded in Lake Tanganyika mussels

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Received: 31 August 2006 – Accepted: 9 September 2006 – Published: 22 September 2006

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Abstract

Biogenic productivity of Lake Tanganyika is highly dependent on seasonal upwellings of anoxic deep waters. We investigated the shell of freshwater bivalve *Pleiodon spekii* as a geochemical archive of these periodic hydrological changes tuned by the monsoon regime. The results of a 2-years-long geochemical survey of the coastal waters performed on the dissolved and particulate fractions were put in perspective against laser ablation ICP-MS profiles of Mn in five aragonitic shells from the same lake location. Skeletal Mn profiles in 3 shells are very similar and dominated by episodic peaks that matched the Mn increase recorded in surface waters during the 2002 upwelling, while a shell collected during 2003 dry season detect both 2002 and 2003 upwelling events. Larger shells showing an extremely reduced growth display more than 8 Mn peaks suggesting at least an 8 years record of seasonal changes in water composition.

1 Introduction

Lake Tanganyika (Fig. 1) is thermally and chemically stratified (Craig, 1974; Plisnier, 1999; Branchu, 2001), and particularly sensitive to climate changes (Cohen et al., 2000; Plisnier et al., 2000). The lake is under a semi-humid tropical climate with a main rainy season from October to April. During the dry season from May to September, the Southeast African monsoon pushes oxic surface waters to the North causing seasonal upwellings of cold, oxygen-depleted, nutrient-rich deep waters at the Lake south end (Coulter, 1991; Plisnier, 1999). A recent warming trend enhanced the density gradient that slowed this vertical mixing and reduced primary production (O'Reilly et al., 2003; Verburg et al., 2003; Alleman et al., 2005), probably impacting pelagic fisheries (Hecky et al., 1981). Recent efforts to model these climatic effects on lake hydrology (Naithani et al., 2003) were limited by our lack of pre-instrumental data. The present contribution aims to investigate how past hydrological information may be ex-

tracted from Tanganyika bivalves' shells.

Accretionary biogenic carbonate has been widely used to evaluate paleoenvironmental conditions as they record chemistry of the environment where it is precipitated. By growing fast, bivalves produce shells of exceptional potential for daily to annual reconstruction of water chemistry and temperature. In temperate freshwater shells Mn offers a robust record of dissolved Mn concentrations (Lindh et al., 1988; Jeffree et al., 1995; Markich et al., 2002). In Lake Tanganyika, seasonal upwellings were expected to supply surface waters with large amount of Mn, which might be recorded in the coastal leaving bivalves. To test and calibrate potential seasonal Mn incorporations in bivalve shells a 2-years Mn survey of lake waters were put in perspective against laser ablation ICP-MS profiles of Mn within five aragonitic shells of *Pleiodon spekii* (Bivalvia, Mutelidae) collected alive at the southern tip of Lake Tanganyika. *P. spekii*, a species endemic to this lake, is particularly suitable because of its wide distribution on the actual near-shore environments but also in both archaeological and geological settings (D. Van Damme, private communication).

2 Materials and methods

2.1 Study site and shell collection

Living *P. spekii* were hand-picked at 5 m depth on the Mbita Island's shore (8°45.226′ S 31°05.148′ E see Fig. 1) near Mpulungu (Zambia) and separated from the pelagic zone by a rocky outcrop. In July 2002, 37 living specimens were collected, measured for shell length, labelled with "bee tags" and put back into the sandy shore. Five shells, were collected: V10, V72 and V22 in March 2003; V-E and V61 in July 2003 and February 2004 respectively. The length growth was slow and therefore imprecise to serve as an appropriate tool to evaluate the shell growth. In contrast, because ageing is accompanied with a strong thickening of shells, we used the weight combined to the length to estimate their relative ages (Fig. 2) (V10<V72≈V-E<V61<V22). Only shell

V10 displayed a significant length increase (2.9 mm/8 month) usable to date the chemical profile. Laser data are given as a function of the distance from the ventral margin. Only two studies have dealt with *P. spekii* (Pain and Woodward, 1964; Kondo, 1986): ecology, life span and growth patterns are mostly unknown. We mainly found groups of large adults specimens (80 mm < length < 180 mm) partly stuck in sediments from 2 to 20 m water depth, but we did not observed juveniles (only two dead specimens < 60 mm), suggesting they are living in another environment (deep waters) to avoid biocorrosion and predation. The posterior end, where reside the siphons, undergoes an active biocorrosion whereas the rest of the shell is protected by the sediment. Large specimens tagged in 2001 were found alive in 2005, indicating a life span of more than 4–5 years. The whole shell is aragonitic as evidenced by X-ray diffractometry on powder samples (XRD). Polished sections of the shell (400 μm thick) were realized in the anterior part (Fig. 1).

2.2 Analytical procedure

Water temperatures were measured biweekly using a Seabird CTD probe at the pelagic site down to 100 m and recorded continuously at the bivalve site using a Tidbit® probe. Pelagic and coastal waters were collected biweekly using Hydrobios bottles, filtered (0.4 μm polycarbonate membranes) and acidified (bi-distilled HNO_3 2%). A deep profile was performed at station 8 in July 2002 (particles) and in February 2004 (filtrated water).

Dissolved Mn (Mn_d) along with dissolved Al (Al_d) and Ca (Ca_d) were analyzed in filtrated waters (0.45 μm) by HR-ICP-MS (Finnigan ELEMENT2) using In and Bi as internal standards. Detection limit (3σ of the blank values) for Al, Ca and Mn was 1.35, 0.77 and 0.07 μg/L respectively. Particles were digested with HCl/HNO_3/HF (3/2/1 vol.) at 90°C in sealed Teflon beakers. After evaporation to dryness, the residue was dissolved in 12 mL of 0.1% HNO_3 Suprapur and the solution analyzed for Al, Ca and Mn by ICP-AES (Thermo Optek Iris Advantage) using Y and Au as internal standards. Detection limit (3σ) for Al, Ca and Mn are 20, 4 and 0.1 μmol.L^{-1} respectively.

In shells, high-resolution (50 μm spots; 25 μm intervals) Mn/Ca determinations were carried out on a laser-ablation inductively coupled plasma-mass spectrometer (LA-ICP-MS, PQ2+, laser 266 nm; operating conditions in Lazareth et al., 2003). Data were calibrated using both the NIST 610 (values from Pearce et al., 1997) and a carbonate reference material USGS MACS1 (values from S. Wilson, USGS, unpublished data, 2004) following Toland et al. (2000) procedure. The laser was shot in the middle nacreous layer spanning about 2 cm, from the edge (newly formed carbonates) to the umbo (Fig. 5a). Toward the umbo, the growth layers become thinner and flatten. Sampling these old parts would lead to a bias by integrating multiple growth layers representing a longer period of calcification. Constant value of $CaCO_3$=99% in weight was assumed over the whole shell section analyzed, as the analysis of the organic matrix on bulk samples of the shell V72 did not exceed 1.1–1.2 dry wt % (F. Marin, private communication). The LA-ICP-MS detection limit for Mn is 11.3 ppm (3σ) and the analytical reproducibility is 1.3% ($2\sigma_M$) (reference material MACS1, n=105, [Mn]=108 ppm). LA-ICP-MS data obtained for shell V10 were validated with solution HR-ICP-MS analysis (Fig. 5b). These analyses were completed on powder samples (~100 μg dissolved in 2%HNO_3 solution) performed along the LA-ICP-MS profile using a 300 μm drill bit fixed to a computer controlled micro positioning device (Merchantek MicroMill™). Carbonates samples were dissolved in 1 mL 2% HNO_3 solution containing 1 ppb of In and Bi, which were used as internal standards. A mineralized natural carbonate (international standard CCH-1) was used as an external standard. The Mn analytical reproducibility is 3.25 % ($2\sigma_M$) (n=16; reference material CCH1, values from Govindaraju, 1994).

3 Results

Water depth chemical profilings from station 8 (Fig. 3) revealed that the oxygenated mixed layer (0 m to 150 m) was depleted in dissolved Mn (Mn_d) (concentrations <6 nmol.L^{-1}) but enriched in particulate Mn (Mn_p) (concentrations >2 nmol.L^{-1}). Below the oxycline (180–200 m), concentrations of Mn_d increased drastically to a maximum

value of 660 nmol.L^{-1} at 200 m in the anoxic, indicative of the reductive dissolution of the oxy-hydroxides particles. Deep water Mn_p concentrations followed an opposite pattern and stabilized at low concentrations <0.5 nmol.L^{-1} from 300 m to 1400 m. During the 2 years monitoring, Mn concentrations in coastal surface waters displayed large variations (1 to 12 nmol.L^{-1}) in the particulate fraction (>0.4 μm) as well as in the dissolved fraction (2 to 45 nmol.L^{-1}) (Fig. 4a). From October 2002 to April 2003 (i.e. the rainy season) a slighter increase of Mn_p occurred simultaneously with a marked increase of Al (Figs. 4a, b). This points to a clear detrital derivation of trace Mn in particles during the rainy season. To correct this detrital inputs, Mn_p contents were normalized to Al contents as Mn/Al ratios. A strong increase of Mn/Al ratio occurred during the dry/cold seasons (July to September 2002 and 2003) and more precisely during the upwelling periods, which are marked by the local cooling of coastal (Fig. 4b) and pelagic (Fig. 4c) waters.

The growth lines, clearly visible under the microscope, allowed a precise fitting of LA-ICP-MS and HR-ICP-MS profiles (Fig. 5a). A strong correspondence exists between both profiles (Fig. 5b; r^2=0.75) considering that each drill sample represents a mean value of about five laser shots. This demonstrates that LA-ICP-MS measurements are robust and relevant as quantitative estimates of the skeleton Mn concentrations. Skeletal Mn profiles are similar for shells V10, V72 and V-E (Fig. 5). All older parts of these 3 shells display similar dissymmetric Mn peaks with maximum values at 261, 204 and 287 ppm respectively, followed by decreasing trends until the collection dates for V10 and V72. At this time, the concentrations are about 40 ppm in the range of those measured before the Mn peak. Superposed to this trend, the skeletal Mn displays a succession of small and short increases, with maximum values not exceeding 120 ppm. Shell V-E, collected in July 2003 during the following dry season, displayed a second Mn peak (379 ppm). According to the shell measurements, the main Mn increase measured on shell V10 extended over 3 weeks with a peak at the end of June 2002.

The larger shells V61 and V22 showed an extremely reduced growth during the length of our survey. In the most recent part of these shells, eight Mn peaks are

similar in shape as well as in amplitude for both specimens. Most of these peaks are dissymmetric and therefore turn out to be very similar to those described for shells V10, V72 and V-E. Mn variations in V34 are superposed to a gradual increase through ontogeny from low values close to 40 ppm in the older parts of the shell to high values close to 200–300 ppm in the most recent layers.

4 Discussion

To properly identify the Mn-oxide related peaks of concentrations, Mn contents were normalized by Al. Coastal water Mn/Al profiles displayed two peaks during the seasonal marked cooling of surface waters, which are known to correspond to upwellings of deeper water. This cooling lasted fifteen days to one month in 2002 (Fig. 4c). In water, it corresponds to the temporal extension of the Mn peaks in particulate (Fig. 4a) and dissolved (not shown) fractions on two consecutive years (2002–2003; Fig. 4a). The timely supply of reduced Mn^{2+} by the anoxic upwelled waters and its subsequent oxidation in high pH (8.4 to 9.2) surface waters could explain the rise of non soluble MnO_2 or $Mn(OH)_x$ particles measured in the epilimnion. Furthermore, the high sunlight intensity may increase the Mn_d residence time in surface waters through both a photo-inhibition of the Mn-oxidizing bacterial activity and enhancement of Mn-oxides dissolution by photoreduction (Sunda and Huntsman, 1994). This may explain the maintenance of a high Mn_d content in surface water during the upwelling period.

Mn skeletal archives fit trends observed in coastal water particles, with peaks coeval to the 2002 and 2003 upwellings and small variations during the rainy season (October 2002 to March 2003). The similarity in Mn profiles from shells V10, V72 and V-E highlights a strong inter-individual reproducibility that is a prerequisite to the use of shell geochemistry in environmental monitoring. In shell V10 where the growth rate has been calibrated, the shell Mn peak is coeval to the Mn singular peak in water. From this, we postulate that in all 3 specimen, the first Mn peak records the same environmental event (i.e. the June–July 2002 upwelling event).

A rapid and positive response of Mn levels in the aragonitic shells of *P. spekii* to the elevation of particulate and/or Mn_d in water is consistent with the freshwater bivalves sensitivity to this element in both temperate and tropical conditions (Carrel et al., 1987; Lindh et al., 1988; Jeffree et al., 1995; Siegele et al., 2001). Such sensitivity is consistent with the very high level of this element in the soft tissues of *P. spekii*, ($6544\,\mu g.g^{-1}$, dry weight) with concentrations of three orders of magnitude higher than those reported for lake fishes (Chale, 2002). In freshwater bivalves, calcification occurs within the extrapallial fluid, which is isolated from the external medium. Mantle secretions mostly contribute to the chemical composition of this fluid from which the mineralization occurs (Wada and Fujinuki, 1976; Wheeler, 1992). Indeed, a well-developed periostracum on freshwater shells constitutes a barrier insolating the extrapallial cavity. Mn could derive from dissolve or particulate sources. According to the Free-Ion activity Model (Campbell, 1995), the reduced Mn (Mn^{2+}), is the most bioavailable form. Rapid and acute biological response (valve movement) of the Australian tropical freshwater unionid *Veselunio angasi* experimentally exposed to elevated concentrations of Mn^{2+} was consistent with this model (Markich et al., 2000). Mn^{2+} transportation through tissues is indeed facilitated by its metabolic and cristallochemic analogy to Ca during its uptake from the aquatic medium (Jeffree and Brown, 1992; Markich and Jeffree, 1994; Markich et al., 2001) and its incorporation into aragonite lattice. However, we disregard such a pathway because we did not succeed to mark the shells with dissolved $MnCl_2$ (Jeffree et al., 1995). Indeed after a marking time of about 12 h, we did not observe any luminescent marking line under cathodoluminescence (Langlet et al., 2006) despite the intense natural Mn-induced cathodoluminescence of Pleiodon shells. In the lack of such a Mn^{2+} incorporation, we rule out the ionic form as the most bioavailable source of skeletal Mn concentrations. Therefore, we postulate that nutrition on Mn-rich particles is the most likely source of Mn in agreement with several other recent investigations. First, it was shown that Bivalves accumulated metal in their tissues from the organic and inorganic components of their diet, actively through digestive processes, and passively through desorption (Arifin and Bendell-Young, 2000). Second, peaks of

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skeletal Mn have been reported for *Mytilus edulis* in temperate marine ecosystem (Vander Putten et al., 2000) and for *Isognomon ephippium* in tropical mangroves (Lazareth et al., 2003). In both cases, peaks were supposed to be related to phytoplankton's blooms and increases of Mn-rich particles rather than a direct uptake of Mn_d. This hypothesis was consistent with the delay of a few weeks observed between the increased run-off of freshwater carrying high contents of nutrients and Mn_d in the tropical estuary and the appearance of high Mn concentrations in *I. Ephippium* (Lazareth et al., 2003). In Lake Tanganyika, supply of nutrients-rich deep waters tuned by the monsoon regime results in a marked increase in algal biomass in the coastal waters as shown by the seasonal narrow chlorophyll-a maxima (Descy and Gosselain, 2004). An increase of biological activity, concomitant with a supply of Mn_d in surface waters likely enhances the production of Mn-rich particles while green algae can efficiently take up and concentrate Mn^{2+} intracellularly (Sunda and Huntsman, 1985). Moreover, photosynthetic activity in dense algal population generates high pH (>9) which in turn favours oxides or carbonates precipitations in organic-rich microenvironments. (Richardson et al., 1988). In shells, the dissymmetry of the Mn peaks is likely the combination of two processes: (1) the relatively short lag time (up to several days) between the exposition to elevated water Mn concentrations and the related increase of Mn/Ca in the shell (Jeffree et al., 1995); (2) the longer time that is needed to re-establish equilibrium between the aquatic medium and the body fluids (Markich and Jeffree, 1994), (Jeffree et al., 1995). Moreover, this delay might be extended by the action of filtration-feeders, which continue to concentrate Mn-rich organic or inorganic particles from the suspended sediments.

For old specimens V61 and V22, if each Mn peak had been recording discrete annual monsoon-related upwelling, we could date back both shells. Mn cycles therefore indicate that the bivalves were at least 8 years old when they were collected. From January 1998 to 2002, the relative intensity and shell length of each peak is equivalent in both shells, with a possible missing peak in 1996 in both specimens. This suggests that Mn in *P. spekii* shells has potential for recording both a seasonal phenomenon related to the upwelling and its relative intensity. Intensity changes may reflect quantitative and

qualitative changes in the particulate load associated to the biological activity in lake water. A more detailed analysis of shell layers including other chemical proxies (such as Sr/Ca, $\delta^{18}O$ and $\delta^{13}C$) coupled with spectral statistical analyses on a large number of specimens would help to determine the factor controlling Mn signature in *P. spekii* to provide long, uninterrupted, seasonally to inter-annually resolved archives of past upwelling events.

5 Conclusions

Mn peaks in Pleiodon shells show a consistent positive relationship with the main increase of Mn-rich particles in surface waters. This event is related to the oxidation and subsequent precipitation of large amount of Mn_d supplied by the upwelling driven by the SW African monsoon. Therefore shell Mn signature should provide a record of short-term environmental changes linked with recent or past mixing events in Lake Tanganyika. A statistical approach conducted on numerous Mn profiles from historical specimens could trace the variations of monsoon effects for the pre- or post-industrial period in Lake Tanganyika, as well as in similar other deep stratified African lakes. This would be extremely useful to reconstruct past century ENSO impacts on African lake upwellings from historical Pleiodon collections.

Acknowledgements. We thank L. Monin and J. Navez for laboratory assistance. We are grateful to A. Bernard (ULB) for providing the XRD data and F. Marin for organic matrix analysis. The Belgian Federal Science Policy Office, Brussels, Belgium, provided funding in the framework of the CLIMLAKE project (PADD II 2001-2005) and Action 1 "Tanganyika project" (2002–2006).

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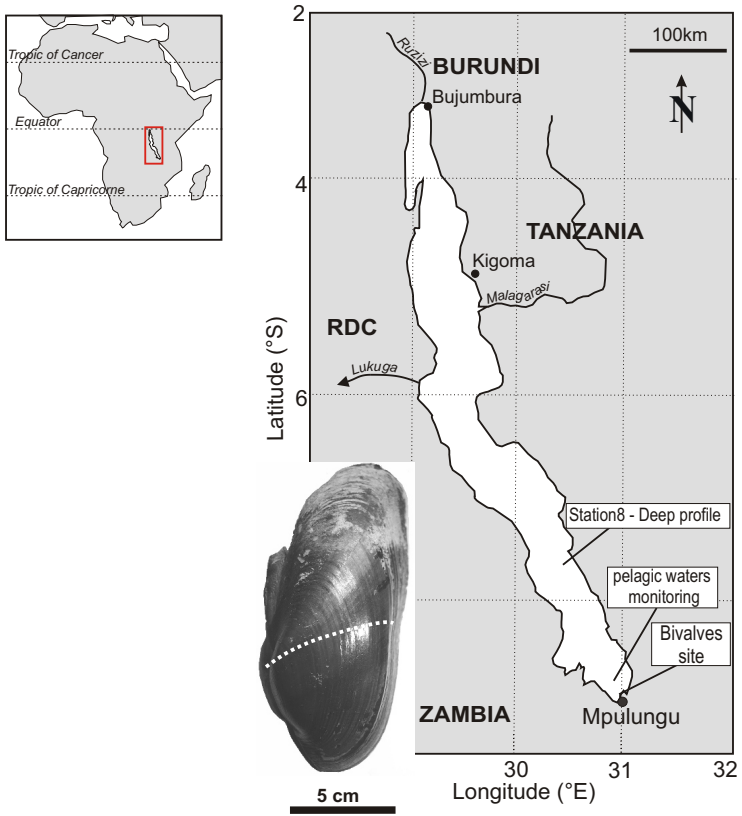

Fig. 1. Location of the study area and sampling sites, in the South of the Lake Tanganyika, where an upwelling occurs seasonally. The lake houses many endemic species such as bivalves *Pleiodon spekii* (inset). Skeletal Mn profiles were done along radial sections in the anterior part of the shell (white doted line) because it is preserved from biocorrosion.

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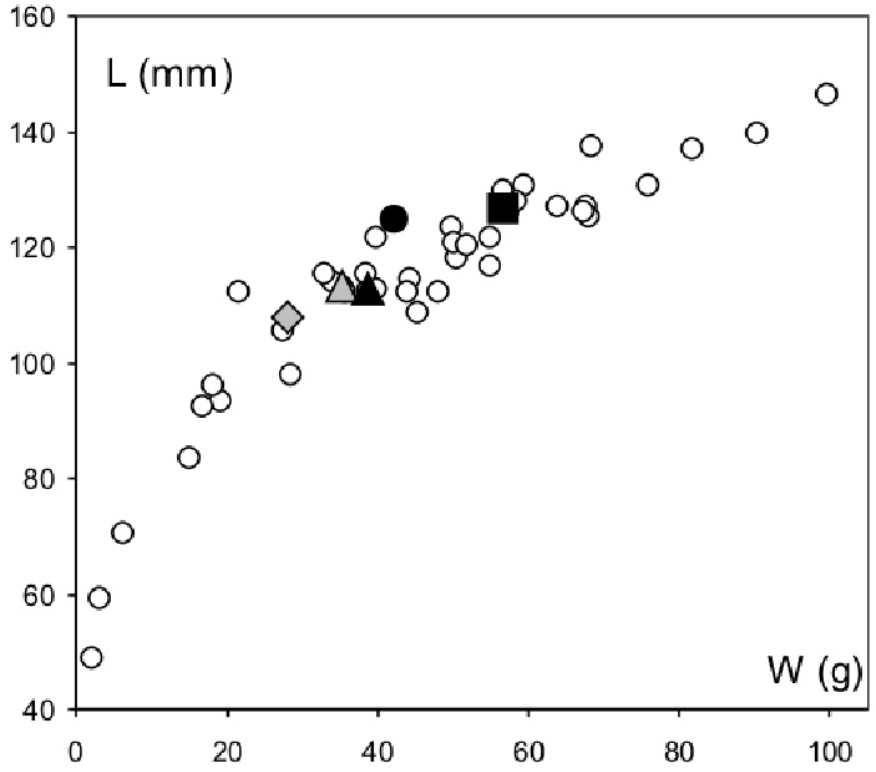

Fig. 2. *Pleiodon spekii*. Shell length (mm) as a function of single valve weight (g). Specimens analyzed: grey lozenge: V10; grey triangle: V72; black triangle: V-E; black circle: V61; black square: V22.

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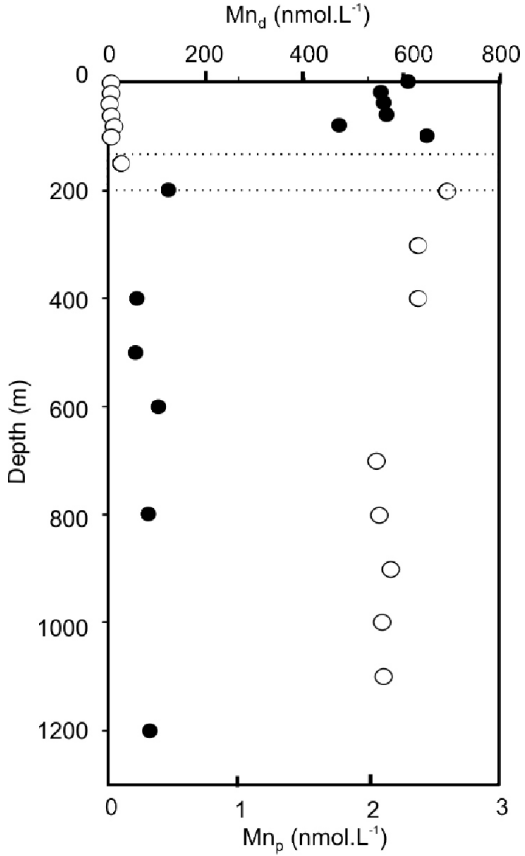

Fig. 3. Typical deep profiles of Mn_d (white dots; nmol.L^{-1}) and Mn_p (black dots; nmol.L^{-1}) from station 8, southern basin of Lake Tanganyika.

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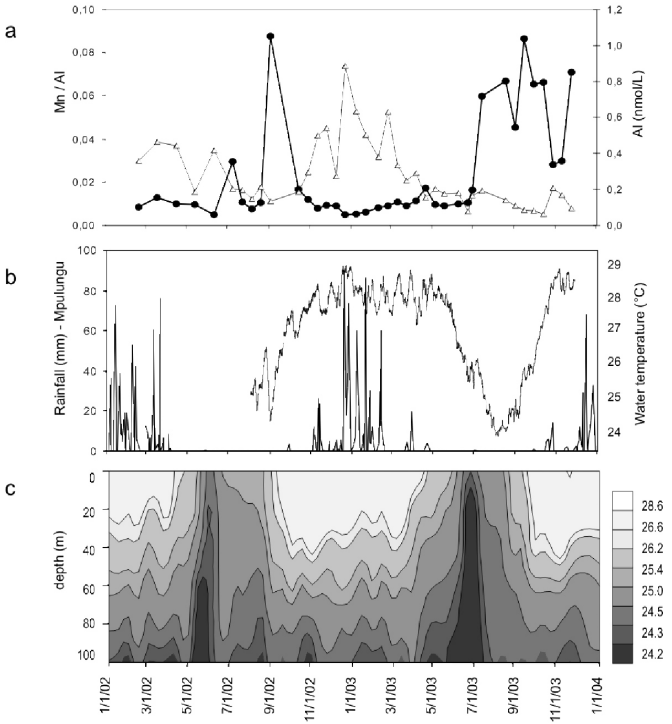

Fig. 4. Results of the 2-years monitoring. Bivalves site (cf. Fig. 1): **(a)** Mn/Al ratio (black dots) and Al concentration (white triangles; nmol.L^{-1}) from the particulate fraction collected below the surface. **(b)** Rainfalls (mm) (Department of Fisheries, Mpulungu) and bottom temperatures (°C). Pelagic site (cf. Fig. 1): **(c)** water temperature from 0 m to 100 m. The seasonality of the thermal structure is well observed. During the rainy seasons (until April 2002 and from October 2002 to January 2003) a thermal stratification occurs. In contrast, a marked surface cooling takes place during the dry season in July–November (2002) and July–October (2003).

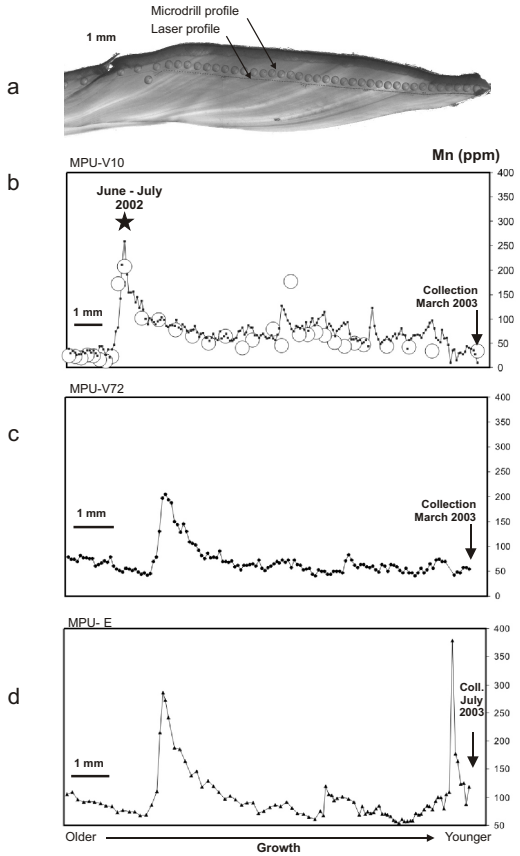

Fig. 5. (a) Shell section showing the sampling profiles in the middle nacreous layer. Microdrill and laser pits are 300 μm and 50 μm in diameter respectively. **(b)** LA-ICP-MS (black squares) and HR-ICP-MS (large circles) Mn profiles on shell V10. **(c, d)** LA-ICP-MS Mn profiles reported for 2 other individuals. For specimen V10, the peak of Mn is dated to June-July 2002 from shell growth length measurements. Scale bar: 1 mm.

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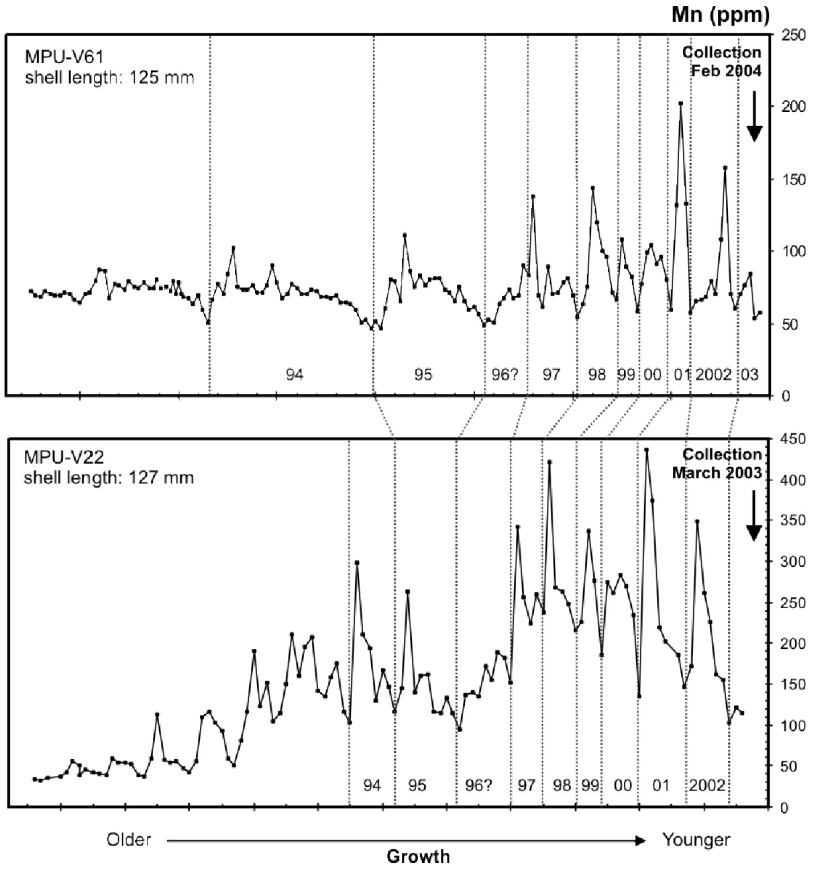

Fig. 6. LA-ICP-MS Mn profiles in 2 large shells. No length increase was measured during the length of our survey. In the most recent secreted shell, 8 peaks are similar in shape as well as in their relative amplitude from one shell to the other.