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Manganese content records seasonal upwelling in Lake Tanganyika mussels

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Abstract. Biogenic productivity of Lake Tanganyika is highly dependent on seasonal upwellings of cold, oxygen-depleted, nutrient-rich 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 three-year-long limnological and geochemical survey of the coastal waters performed on the dissolved and particulate fractions were compared to LA-ICP-MS profiles of Mn in five aragonitic shells from the same lake location. Three shells present very similar Mn/Ca profiles dominated by a peak that matched the concomitant increase of Mn and chlorophyll *a* 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/Ca peaks suggesting at least an 8-year-record of seasonal changes in water composition. We postulate that Mn/Ca in shells record the conjunction of an increase of biological activity with supplied of dissolved Mn and nutrients in coastal waters, resulting in an enhanced assimilation of biogenic Mn-rich particles. By combining the most recent generation of laser ablation system and the powerful High Resolution ICP-MS, the spatial resolution could be improved down to 5 to 10 μm crater size and end up in a better constrain of the relative variations of the annual Mn peaks. Such an approach on *P. spekii* from Lake Tanganyika has definitively a great potential to provide recent and past records on primary productivity associated with the monsoon climate system.

ularly sensitive to climate changes (Cohen et al., 2000; Plisnier et al., 2000). The climate in the lake area is semi-humid 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 extracted from Tanganyika bivalves' shells.

Accretionary biogenic carbonate has been widely used to evaluate paleoenvironmental conditions as its precipitation may record chemistry of the environment. Bivalves produce shells of exceptional potential for daily to annual reconstruction of water chemistry and temperature. Manganese concentrations in temperate freshwater shells offer a robust record of dissolved Mn concentrations (Mn_d) in water (Lindh et al., 1988; Jeffrey et al., 1995). In Lake Tanganyika, seasonal upwellings were expected to supply surface waters with a large amount of (Mn_d), which might be recorded in the coastal living bivalves. To test and calibrate potential seasonal Mn incorporations in bivalve shells a 3-year limnological survey of lake waters was compared to high-resolution Mn/Ca profiles performed by laser ablation ICP-MS from five aragonitic shells of *Pleiodon (Cameronia) spekii* (Bivalvia, Mutellidae) collected alive at the southern tip of Lake Tanganyika. The species is endemic to the lake Tanganyika and particularly suitable both for its wide distribution on the actual near-shore environments and archaeological and geological settings (Van Damme, D., personal communication).

1 Introduction

Lake Tanganyika (Fig. 1) is thermally and chemically stratified (Craig, 1974; Plisnier, 1999; Branchu, 2001), and partic-

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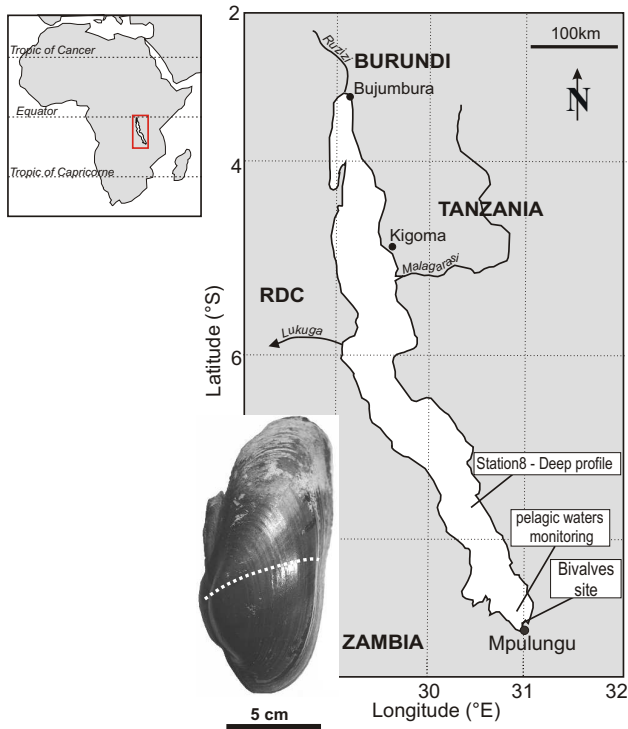


Fig. 1. Location of the study area and sampling sites in the South of the Lake Tanganyika, where an upwelling occurs seasonally. The lake houses many endemic species such as bivalves *Pleiodon spekkii* (inset). Skeletal Mn profiles were done along radial sections in the anterior part of the shell (white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

2 Materials and methods

2.1 Study site and shell collection

Living *P. spekkii* were hand-picked at a depth of 5 m on the Mbita Island's shore ($8^{\circ}45.226' S$ $31^{\circ}05.148' E$ see Fig. 1) near Mpulungu (Zambia) where they were 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. Only two studies have dealt with *P. spekkii* (Pain and Woodward, 1964; Kondo, 1986): ecology, life span and growth patterns are mostly unknown. We mainly found groups of large adults specimens ($80 \text{ mm} < \text{length} < 180 \text{ mm}$) partly stuck in sediments from 2 to 20 m depth, but we did not observe juveniles (six empty shells $< 80 \text{ mm}$) suggesting that they may have an infaunal mode of life to avoid biocorrosion and predation. The posterior end, where the siphons are situated, undergoes an active biocorrosion whereas the rest of the shell is protected by the sediment. Large specimens tagged in 2001 were found alive in 2006, indicating a life span of

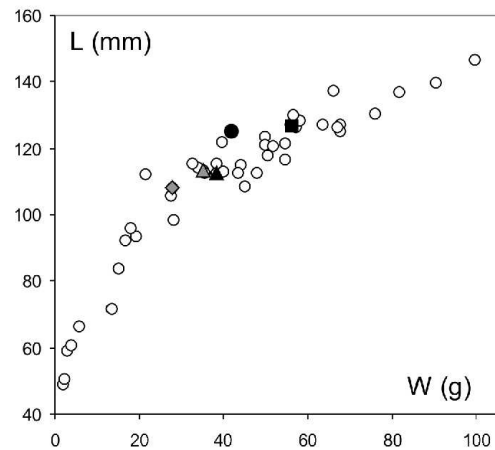


Fig. 2. *Pleiodon spekkii*. Shell length (mm) as a function of single valve weight (g). Specimens analyzed: gray lozenge: V10; gray triangle: V72; black triangle: V-E; black circle: V61; black square: V22.

more than 5 years. The whole shell is aragonitic as evidenced by X-ray diffractometry on powder samples (XRD). Polished sections of the shell ($400 \mu\text{m}$ thick) were achieved in the anterior part (Fig. 1).

Growth pattern of *P. spekkii* was expected to be determined by repeated size measurements of tagged specimens over the two-year survey. However, it remains imprecise because of the extremely sluggish growth of the specimens collected. Except for one specimen, the shell length increases over an 8-month interval between two visiting missions was not large enough compared to the precision of the measurement (caliper). Since we did not find juveniles and because neither biological nor ecological study do exist, we were unable so far to submit a reference growth curve for this species. However since ageing is accompanied with a strong thickening of shells, we could give a relative age by using the length/weight curve (Fig. 2) (the 3 individuals V10, V72 and V-E are younger than V61 and V34). Only shell V10 displayed a significant length increase ($7.6 \text{ mm}/8 \text{ month}$) that could be used for dating the chemical profile. The temporal framework in which geochemical profiles could be interpreted was only deduced from one shell measurements (V10) and the analogy between Mn/Ca variations in shells and in water. Laser data are given as a function of the distance from the ventral margin.

2.2 Staining experiment

As growth patterns remain unknown, a staining experiment with manganese chloride ($\text{MnCl}_2, 4\text{H}_2\text{O}$) was attempted in order to create a luminescent line that would constitute a clear temporal mark in the shell. In July 2002, 13 individuals were put in a bath in which manganese chloride ($\text{MnCl}_2, 4\text{H}_2\text{O}$) was added at 25 ppm (Mn^{2+}). Because of

local constrains, the staining time was limited to 12 hours. Shells were put back to the site for 8 months. In March 2003 all specimens were retrieved and we carried out a second experiment. Ten days after, five specimens (including shell V10) were sacrificed and shells sections were prepared for analysis by cathodoluminescence (CL) (Langlet et al., 2006).

Pleiodon shells presented contrasts of CL with in general high CL intensity in older parts of the shells that could indicate an ontogenic increase of Mn with age. No luminescent line attributed to our staining experiment was observed. Three factors could have combined their effects to bias the staining procedure. (1) The individuals may have failed to grow new shell layers during the staining experiment, due to stress or sluggish growth. (2) Mn should have been incorporated in growth layers but the resulting low CL intensity (low concentrations and/or to thin lines) might be under the detection limit of the technique used (i.e. “cold-cathode”). (3) Another factor could be metabolic. A staining time longer than 12 h in elevated concentrations of Mn might be required to mark *Pleiodon* shells. Indeed, a lag phase and equilibration period up to several days was reported for the freshwater bivalve *Hyridella depressa*, which was experimentally exposed to elevated water concentrations of Mn^{2+} (20 ppm) for 2 to 6 days (Jeffree et al., 1995). In freshwater bivalves the extrapallial fluid is isolated from the external medium, and a substantial regulation of the trace metal transport would lead to reduce efficiency of the Mn-marking compared to marine bivalves (Hawkes et al., 1996; Langlet et al., 2006). In the specific case of *P. spekii* the regulation should be high, Mn being sequestered in soft tissues at very high concentrations ($6544 \mu\text{g}\cdot\text{g}^{-1}$, dry weight) compared to the shell (Chale, 2002). For instance, concentrations in *P. spekii* tissues are two orders of magnitude higher than those reported for the mangrove oyster *Crassostrea rhizophorea* ($61 \mu\text{g}\cdot\text{g}^{-1}$, dw) known for its strong Mn accumulation pattern (Silva et al., 2006). An injection method directly in the pallial cavity or better in the extrapallial fluid cavity may be more efficient to mark the shell, reducing the time for an active sequestration of Mn in soft tissues before being released in the mineralization fluid (extrapallial fluid).

2.3 Analytical procedure

Water temperatures were measured biweekly using a Seabird CTD probe at the pelagic site down to 100 m and at the bivalve site below the surface (1 m depth). The pelagic temperature record covers the entire period from 29 January 2002 to 30 December 2005 whereas the coastal temperature record extends from 29 January 2002 to 5 April 2004. Data on chlorophyll *a* from the biweekly monitoring (bivalve site) were provided by the CLIMLAKE project. Details procedure for pigment extraction and analysis are found in Descy et al. (2000).

Pelagic and coastal waters for geochemical analysis were collected biweekly using Hydrobios bottles, filtered ($0.4 \mu\text{m}$

polycarbonate membranes) and acidified (bi-distilled HNO_3 2%). Filtered water and the related dried filters were stored in deep freezers in Mpulungu, Department of Fisheries, before being transported to Belgium for analysis. Dissolved Mn (Mn_d) along with dissolved Al and Ca were analyzed in filtered waters ($0.45 \mu\text{m}$) 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 18.5 nmol/L , $0.15 \mu\text{mol/L}$ and 1.24 nmol/L respectively. Particles were digested with $\text{HCl}/\text{HNO}_3/\text{HF}$ (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 19.8 , 4.1 and $0.1 \mu\text{mol/L}$ respectively. The data set concerning the particulate fraction of lake surface water extends from February 2002 to December 2003. The Mn_d series extends from March 2003 to October 2004 (missing points between December 2003 and March 2004). Only few Mn_d data were available for the year 2002 due to storage problems in Mpulungu. Afterwards, the monitoring of both dissolved and particulate fraction was successful between March and December 2003.

In shells, high-resolution ($50 \mu\text{m}$ spots; $25 \mu\text{m}$ intervals) Mn/Ca determination was 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) 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. 4a). Toward the umbo, the growth layers become thinner and flatter. 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, personal communication). The LA-ICP-MS detection limit for Mn is 8.75 ppm (3σ) and the analytical reproducibility is 1.4% ($2\sigma_M$) (reference material MACS1, $n=120$; mean value 0.20 mmol/mol Mn/Ca; recommended value 0.22 mmol/mol). LA-ICP-MS data obtained for shell V10 were validated with solution HR-ICP-MS analysis (Fig. 4b). These analyses were completed on powder samples ($\sim 100 \mu\text{g}$ dissolved in 2% HNO_3 solution) performed along the LA-ICP-MS profile using a $300 \mu\text{m}$ drill bit fixed to a computer controlled micro positioning device (Merchantek MicroMillTM). 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

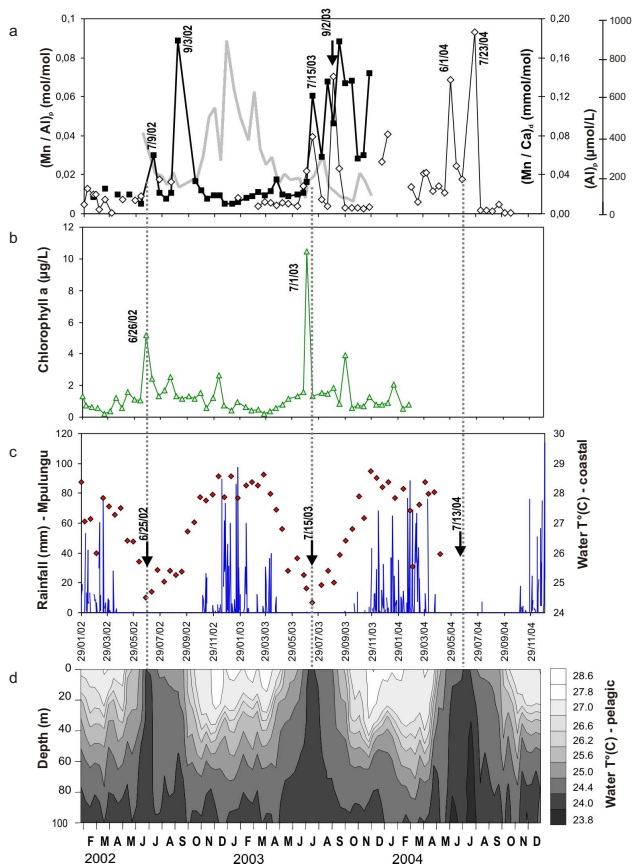


Fig. 3. Results of the 3-year monitoring. Biweekly monitoring at the bivalves site (cf. Fig. 1): **(a)** Water geochemistry: $(Al)_p$ concentrations (gray line; $\mu\text{mol/L}$) and $(Mn/Al)_p$ ratio in the particulate fraction and $(Mn/Ca)_d$ ratios in the dissolved fraction (open diamonds); **(b)** Chlorophyll *a* ($\mu\text{g/L}$); **(c)** bottom water temperatures ($^{\circ}\text{C}$). Rainfalls (mm) data were provided by the Department of Fisheries, Mpulungu. Pelagic station: **(d)** water temperature from 0 m to 100 m ($^{\circ}\text{C}$). The seasonality of the thermal structure is well observed. During the rainy seasons (from October to April) a thermal stratification occurs. In contrast, a marked surface cooling takes place during the dry season in July–August (2002), June–September (2003) and May–September 2004.

natural carbonate (international standard CCH-1) was used as an external standard. The Mn analytical reproducibility is 3.28% ($2\sigma_M$) ($n=16$; reference material CCH1, values from Govindaraju, 1994).

3 Results

3.1 Water monitoring

The biweekly monitoring of temperature at the bivalve site (Fig. 3c) shows the succession of warm rainy seasons (October to April) and cold dry seasons (April to September). The most pronounced surface cooling that signs the maximum in-

tensity of the upwelling event, occurred on 25 June 2002, on 15 July 2003 and on 13 July 2004 in coastal waters (Fig. 3c), according to the pelagic record (Fig. 3d).

In the particulate fraction ($>0.4 \mu\text{m}$), Mn_p displayed large variations (1 to 12 nmol/L) during the dry season 2002 and 2003, but slight increases also occurred during the rainy season (October 2002 to April 2003) (concentration data not shown: see Mn/Al) simultaneously with a marked increase of Al (gray line; Fig. 3a). This suggests a clear detrital derivation of Mn in particles during the rainy season. To correct this detrital inputs, Mn_p contents were normalized to Al contents as $(Mn/Al)_p$ ratios (Fig. 3a). A strong increase of $(Mn/Al)_p$ occurred during the dry season (July to September 2002 and 2003) and is characterized by two peaks in 2002 and several peaks in 2003.

In the dissolved fraction of coastal surface waters, there is a clear seasonal contrast of Mn_d with a sustained increase during the dry season 2003 and 2004. To be consistent with shell data (given as Mn/Ca ratios), the results of dissolved fraction analysis are given as $(Mn/Ca)_d$ molar ratios (Fig. 3a). Ratio values rose from 0.01 to 0.08 in July 2003 and 0.14 in September 2003, and from 0.02 to 0.14 in June 2004 and 0.19 in July 2004. As for $(Mn/Al)_p$, dissolved Mn typically displayed a bimodal peak pattern. The second peak is more intense than the first one although it was not concordant with the most pronounced water-cooling. In the dissolved fraction, both peaks are delayed by about 1.5 month.

3.2 Shell chemistry

The growth lines, that are clearly visible under the microscope, allowed a precise fitting of the laser profile (LA-ICP-MS analysis) to the MicroMill profile (SN-HR-ICPMS analysis) (Fig. 4a). A strong correspondence exists between both profiles (Fig. 4b; $r^2=0.75$) considering that each drill sample represents a mean value of about five laser shots. All MicroMill analysis but one fit the laser profile. This probably results from the presence of a small Mn-rich impurity, which was not sampled at the higher spatial resolution performed by the laser ablation. This demonstrates that LA-ICP-MS measurements are robust and relevant as quantitative estimates of the skeleton Mn concentrations.

Skeletal Mn/Ca profiles are similar for shells V10, V72 and V-E (Fig. 4). All older parts of these 3 shells display similar dissymmetric Mn/Ca peaks with maximum values at 0.47, 0.37 and 0.52 respectively, followed by decreasing trends until the collection dates for V10 and V72. At this time, the Mn/Ca ratio are in the range of those measured before the main peak (0.1). Surimposed to this trend, the skeletal Mn/Ca displays a succession of small and short increases, with maximum values not exceeding 0.2. Shell V-E, collected in July 2003 during the following dry season displayed a second Mn peak (0.69 ppm). According to the shell measurements, the peak measured on shell V10 extended on 3 weeks with a peak at the end of June 2002. The larger shells

Table 1. *Pleiodon spekkii*. Relative variations of the last eight $(\text{Mn}/\text{Ca})_{\text{shell}}$ peaks (i.e. ratio between maximum value and the lowest value preceding each peak) from the ventral margin to the umbo on shell V61 and V22 (Fig. 5). A year was attributed to each peak based on the hypothesis of an annual Mn cycle in shell.

	shell V61	shell V22	% of variation
peak #1 (2002)	2.41	2.37	2%
peak #2 (2001)	3.36	3.33	1%
peak #3 (2000)	1.63	1.53	6%
peak #4 (1999)	1.66	1.59	4%
peak #5 (1998)	2.6	1.79	31%
peak #6 (1997)	1.45	1.14	21%
peak #7 (1996)	2.08	2.21	6%
peak #8 (1995)	2.5	2.28	9%

V61 and V22 (Fig. 5) showed an extremely reduced growth during the length of our survey. In the most recent part of these shells, eight Mn/Ca peaks are similar in shape for both specimens although the ratios values are very different. The relative variations of content (i.e. the ratio between the lowest and the largest value of each peak) are quite similar in the last 8 Mn cycles (Table 1). 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 0.1 in the older parts of the shell to high values close to 0.8 in the most recent layers.

4 Discussion

4.1 Precipitation and dissolution of Mn supplied by the upwelling

The sustained increase of Mn in the dissolved fraction (expressed as Mn/Ca in water) as well as the non-detrital fraction of particulate Mn (increase of Mn/Al ratio) occurred with the marked surface cooling. This supports the idea that large amounts of reduced Mn^{2+} are seasonally upwelled from deep anoxic layers becoming available for biological assimilation by phytoplankton and filter-feeders bivalves. The timely supply of 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 $(\text{Mn}/\text{Al})_p$ in the epilimnion. The general pattern for $(\text{Mn}/\text{Ca})_d$ or $(\text{Mn}/\text{Al})_p$ however consists in two peaks, the second one being more intense although occurring after the most pronounced water cooling (Fig. 3a).

The occurrence of a second peak might result from periodic internal waves that favor pulsed transport through the thermocline, beside the seasonality and inter-annual variability (Plisnier et al., 2001; Naithani et al., 2003). When the

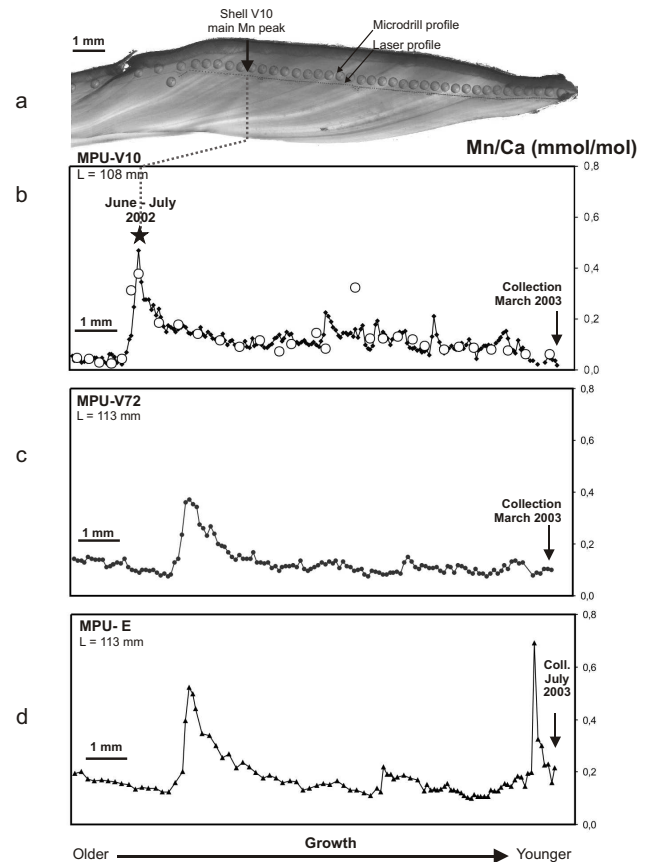


Fig. 4. *Pleiodon spekkii*. (a) Shell section showing the sampling profiles in the middle nacreous layer. Microdrill and laser pits are $300\ \mu\text{m}$ and $50\ \mu\text{m}$ in diameter respectively. (b) LA-ICP-MS (black squares) and SN-HR-ICP-MS $(\text{Mn}/\text{Ca})_{\text{shell}}$ profiles on V10 (circles). For this specimen, the peak of $(\text{Mn}/\text{Ca})_{\text{shell}}$ is dated to June–July 2002 from shell measurements. (c, d) LA-ICP-MS $(\text{Mn}/\text{Ca})_{\text{shell}}$ profiles reported for 2 other individuals. Scale bar: 1 mm. L: length of the shell (mm).

monsoon winds stop (October), the thermocline oscillates between S and N (October to April), conveying higher up nutrient-rich water and probably Mn-rich particles that were sedimenting in the water column throughout the lake. Moreover, although reduced Mn^{2+} is not thermodynamically stable in oxic conditions, a lag time is very likely between its supply from deep layers and its precipitation in surface layers because at least six biogeochemical processes could disturb Mn precipitation and dissolution. (1) High sunlight intensity on lake Tanganyika should affect directly the Mn^{2+} concentration in the surface water by photo-inhibiting the manganese oxidizing micro-organisms (Sunda and Huntsman, 1990). (2) Sunlight has also been shown to exert a stimulatory effect on the reductive dissolution of Mn natural oxides produced by the microbial activity in seawater (Sunda and Huntsman, 1994). (3) The increase of primary production during the dry season should increase the activity

of heterotrophic bacteria that catalyze the reduction of Mn-oxides (non soluble MnO_2 or $\text{Mn}(\text{OH})_x$) as a source of oxygen for decaying the organic matter (Souchu et al., 1998). These conditions favor the reduction and the dissolution of the Mn-oxides or Mn^{2+} bounded to biological debris. (4) By contrast, 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). (5) Moreover, photosynthetic activity in dense algal population generates high pH (>9) which, in turn, favors oxides or carbonates precipitations in organic-rich microenvironments (Richardson et al., 1988). (6) Finally, the nutrient supply from deep layers during the dry season may also enhance the precipitation of Mn-phosphates and carbonates (MnHPO_4 and MnCO_3) (Branchu, 2001).

The differences in the shape and in the amplitude of $(\text{Mn}/\text{Al})_p$ variations during the dry season 2002 and 2003 (Fig. 3a) may be due to differences in the related upwelling. Water temperature in pelagic area (Fig. 3d), air temperature, wind speed monitoring and main nutrients concentration (Descy et al., 2005; data not shown) indicate that the upwelling event was more intense in 2003 than in 2002. For instance, the major increase of Chl *a* in 2003 (Fig. 3b) was higher than in 2002 in response to the higher nutrient supply. A relatively high secondary Chl *a* peak occurred in 30 September 2003, at the end of the dry season and could account for the maintenance of high $(\text{Mn}/\text{Al})_p$ levels for a few months after the 2003 upwelling.

4.2 Phytoplankton blooms as a source of bioavailable Mn?

In shell V10 where the growth rate has been calibrated, the shell Mn peak is coeval to the first Mn increase in dissolved and particulate fractions (Fig. 4). 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 study. From this, we postulate in all 3 specimens, that the first Mn peak represents a record of 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. spekkii* to the elevation of Mn 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). With a very high level of Mn in its soft tissues ($6544 \mu\text{g}\cdot\text{g}^{-1}$, dry weight), *P. spekkii* confirms such a sensitivity with Mn concentrations three orders of magnitude higher than those reported for lake fishes (Chale, 2002). According to its capacity of Mn bioaccumulation, we hypothesize that the 6 to 20 fold increase of $(\text{Mn}/\text{Ca})_d$ in surface water (Fig. 3a) are large enough to induce the 3 to 4 fold increase of $(\text{Mn}/\text{Ca})_{\text{shell}}$.

In freshwater bivalves, a well-developed periostracum closes the extrapallial cavity and isolates the mineralization fluid from the external medium. Mantle secretions mostly contribute to the chemical composition of this fluid (Wada and Fujinuki, 1976; Wheeler, 1992). The Mn transported through the tissues and incorporated in shells could derive from dissolved (reduced Mn^{2+} forms) or particulate sources (inorganic and biogenic particles). According to the Free-Ion activity Model (Campbell, 1995), the reduced form of manganese is the most bioavailable form. Rapid and acute biological response (valve movement) of the Australian tropical freshwater unionid *Veselumio angasi* experimentally exposed to elevated concentrations of Mn^{2+} was consistent with this model (Markich et al., 2000). The transportation of Mn^{2+} through tissues should be facilitated by its analogy to Ca during uptake from the aquatic medium (Jeffree and Brown, 1992; Markich and Jeffree, 1994; Markich et al., 2001). However, bimodal pulses of $(\text{Mn}/\text{Ca})_d$ in coastal surface waters during the dry seasons (Fig. 3a) could not properly explain the single peak observed in shells, indicating that the $(\text{Mn}/\text{Ca})_d$ composition of water is not the sole factor controlling skeletal Mn.

Particulate sources of Mn should be available as bivalves accumulate 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). However, the peak of $(\text{Mn}/\text{Ca})_{\text{shell}}$ cannot be simply explained by the bimodal pattern of total Mn_p variations. An alternative hypothesis takes into account the Mn reservoir associated with phytoplankton blooms, i.e. biogenic particle rather than total Mn_p , in agreement with several other recent investigations. Peaks of skeletal Mn have been reported for *Mytilus edulis* (Vander Putten et al., 2000) in temperate marine ecosystem 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 observed delay of a few weeks 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 the South of Lake Tanganyika, the major increase of Chl *a* (i.e. phytoplankton biomass estimation) occurred right from the start of the upwelling with an apex on 26 June 2002 and on 1 July 2003 (Fig. 3b) as main nutrients (N, P and Si) are increasing 2 to 3 times depending on the strength of the upwelling (Descy et al., 2005; data not shown). It illustrates the high reactivity of the phytoplankton to the rapid increase of limiting nutrients in Lake Tanganyika surface waters. These findings suggest a relationship between primary production and increased incorporation of Mn into the shell. This hypothesis seems plausible, as natural phytoplankton blooms have been shown to be associated with an increase in suspended particulate Mn (Sunda and Huntsman, 1994). 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). We postulate that $(Mn/Ca)_{shell}$ is controlled by the conjunction of a biological activity increase and a supply of Mn_d , resulting in an enhanced assimilation of Mn-enriched digestible food particulate by the bivalve. These conditions are present during the dry season, especially at the beginning of the upwelling, but not in the rest of the year. The possibility of multiple $(Mn/Ca)_{shell}$ peaks per year cannot be precluded of the lack of any time marker in shells, but this option is unlikely if we consider shell V10 for which current preliminary results confirm our time scale estimates. Further studies on the relationship between Mn and phytoplankton and on the physiological influences on Mn incorporation are required to verify if skeletal Mn could be used as a quantitative proxy of primary production. Finally, the dissymmetry of the $(Mn/Ca)_{shell}$ peaks is likely the combination of three processes: (1) the relatively short lag time (up to several days) between the exposure to elevated water Mn concentrations and the related increase of $(Mn/Ca)_{shell}$ (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), (3) the extension of this delay by the action of filtration-feeders, which continue to concentrate Mn-rich organic or inorganic particles from the suspended sediments.

4.3 Manganese cycles in old shells

The overall Mn patterns in older specimens V61 and V22 (Fig. 5) are similar, despite differences in the concentrations levels and the ontogenic trends. Indeed, the relative variations of content are quite similar in the last 8 Mn cycles (see Table 1). It supports the idea that skeletal Mn is a potential proxy of the primary production in relation with limnological changes in surface waters. If each Mn peak is supposed to record annual monsoon related upwellings, we could then date back both shells. Manganese cycles may therefore indicate that both bivalves were at least 8 years old when they were collected. The comparison of the area under the $(Mn/Ca)_{shell}$ curves may give some hints on how shell data could be quantified and then used as a quantitative proxy. However, even if such investigations are promising, we are limited by the actual resolution of the laser ($50 \mu m$) that gives us too few analyses by peak to be reliable. The improvement of the laser methodology with more energetic beam (for instance the 157 nm LA-ICP-MS) and a more sensitive mass spectrometer may allow future use of surface peak measurements as a mean to quantify relative change in the upwelling intensity. At the moment, one can only speculate on the nature of additional “vital effects” varying with age and controlling Mn incorporation in shell. First, age-mediated changes in the metabolic activity might be in-

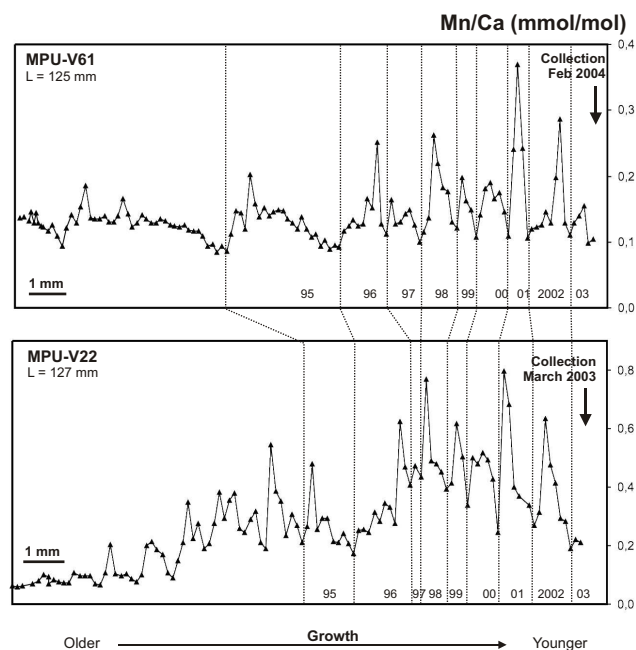


Fig. 5. *Pleiodon spekkii*. LA-ICP-MS $(Mn/Ca)_{shell}$ profiles in 2 large shells. No length increase was measured during our survey. The last 8 peaks are similar in shape as well as in their relative amplitude from one shell to the other, although the concentrations are different. Scale bar: 1 mm. L: length of the shell (mm).

involved in the ontogenic trend observed for skeletal Mn in *P. spekkii*. Rosenberg and Hugues (1991) noted that Mg/Ca composition within the shell of *Mytilus edulis* increased with the shell curvature, since the metabolic efficiency decreased. They proposed that a metabolic gradient could control the shell geochemistry and contribute to the control of the shape. Second, detoxification processes in soft tissues may become less efficient with age leading to the sequestration of increasing quantity of Mn in the shell. Third, it is also possible that gametogenesis and energy relocation for spawning may influence Mn/Ca ratios in shells. As the biology of *P. spekkii* is unknown, we cannot give any indication about the age from which shells become sexually mature and about the reproduction patterns (continuous spawning vs. seasonal spawning). Finally, a detailed analysis of shell isotopic composition ($\delta^{18}O$ 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. spekkii* to provide long, uninterrupted, seasonally to inter-annually resolved archives of past upwelling events.

5 Conclusions

The consistent positive relationship between $(Mn/Ca)_{shell}$ peaks in Lake Tanganyika mussels and the concomitant increase of chlorophyll *a* and manganese in surface waters

during the seasonal upwelling suggests that $(\text{Mn}/\text{Ca})_{\text{shell}}$ could be controlled by the assimilation of biogenic Mn-rich digestible particles. Therefore shell Mn should provide a record of short-term environmental changes linked with recent or past mixing events driven by the SE African monsoon in Lake Tanganyika. Further studies should test if skeletal Mn could be used as a quantitative proxy of primary production. 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 deep stratified African lakes. This would be extremely useful to reconstruct pluri-annual climatic related variations such as ENSO events over the past century from historical bivalve collections.

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