Manganese incorporation in living (stained) benthic foraminiferal shells: A bathymetric and in-sediment study in the Gulf of Lions (NW Mediterranean).

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Abstract

Manganese geochemistry in deep-sea sediments is known to vary greatly over the first few centimeters, which overlaps with the in-sediment depth habitats of several benthic foraminiferal species. Here we investigated manganese incorporation in benthic foraminiferal shell carbonate across a 6-station depth transect in the Gulf of Lions, NW Mediterranean to unravel the impacts of foraminiferal ecology and Mn pore water geochemistry. Over this transect water depth increases from 350 to 1987 m, while temperature (~13˚C) and salinity (~38.5) remained relatively constant. Manganese concentrations in the tests of living (Rose Bengal stained) benthic foraminiferal specimens of *Hoeglundina elegans*, *Melonis barleeanus, Uvigerina mediterranea*, *Uvigerina peregrina* were measured using laser ablation inductively coupled mass spectrometry (laser ablation ICP-MS). Pore water manganese concentrations show a decrease from shallow to deeper waters, which corresponds to a generally decreasing

organic matter flux with water depth. Differences in organic matter loading at the sediment water interface affects oxygen penetration depth into the sediment and hence Mn pore water profiles. Mn/Ca values for the investigated foraminiferal species reflect pore water geochemistry and species-specific microhabitat in the sediment. The observed degree of variability within a single species is in–line with know ranges in depth habitat and gradients in redox conditions. Both Mn/Ca ratio and inter-specific variability hence reflect past Mn cycling and related early diagenetic processes within the sediment, making this a potential tool for bottom-water oxygenation and organic-matter fluxes. Dynamics of both in-sediment foraminiferal depth habitats and Mn cycling, however, limit the application of such a proxy to settings with relatively stable environmental conditions.

1. Introduction

Reconstructing past climate and environmental change largely depends on so-called proxies. These proxies relate measurable variables in the geological record to target parameters, such as e.g. temperature, biological productivity and bottom water oxygenation. The carbonate shells of unicellular protists, foraminifera, are one of the most utilized signal carriers for reconstructing past environments. Both the census data of foraminifera and the geochemical composition of the shells are used in this context. The geochemical composition of the shells is investigated for their stable isotopic composition as well as for their trace and minor element incorporation. Both pelagic and bottom water conditions are reconstructed this way, using planktonic and benthic foraminiferal species respectively.

Most existing calibrations of trace element uptake in foraminiferal test carbonate are based on comparing their composition with bottom water conditions

(Elderfield et al., 2006; Nürnberg et al., 1996; Yu and Elderfield, 2007). Many benthic foraminiferal species live, however, within the sediment and precipitate their calcium carbonate test in contact with pore water. As a result, the trace metal composition of pore water exerts a control on the uptake of trace metals in their test. This effectively links benthic foraminiferal microhabitat preference and pore water chemistry. On the one hand, this creates complications when using foraminiferal trace metal ratios for reconstructing bottom water conditions, whereas on the other hand, it offers the possibility to develop proxies of pore water chemistry in the past.

Linking foraminiferal test chemistry with pore water chemistry requires in-depth knowledge of, 1) how early diagenesis in sediments affects pore water chemistry, 2) the habitat preference of the foraminiferal species, 3) foraminiferal migration (and the depth at which they calcify) within the uppermost sediment layer. In principle, the chemical composition of living (stained) benthic foraminifera will reflect all these processes.

For many elements an important inter-specific difference in uptake of trace metals has been observed (Hintz et al., 2006; Wit et al., 2012; Barras et al., 2018), a so-called vital effect. This implies that in addition to ecology and pore water geochemistry, trace metal partitioning also needs to be taken into consideration. This requires a comparative study between locations where all three of these aspects have been quantified.

Reconstructing past pore water trace metal profiles is important since it provides valuable information on organic carbon degradation and recycling of nutrients at the seafloor (Van Cappellen and Wang, 1996; De Lange, 1986). Such diagenetically controlled trace metal profiles are used in quantitative models constraining oceanic

81 carbon fluxes and burial (Wang and Van Cappellen, 1996). Knowledge of such profiles
82 in the past could thus help to reconstruct past carbon cycles.

83 Benthic foraminiferal species have a specific preference for their depth-habitat
84 (Jorissen et al., 1995). Some benthic foraminiferal species are limited to a very narrow
85 environmental in-sediment range, for example, along redox fronts, whereas others have
86 a wider distribution, thriving under variable conditions and consequently occupy a
87 broader niche. These differences in depth-habitat preferences could be related to the
88 presence of different types of metabolism (Koho et al., 2011; Risgaard-Petersen et al.,
89 2006). As such, trace metal profiles and foraminiferal in-sediment depth habitat can be
90 related, such as recently proposed in a conceptual (TROXCHEM^3) model for the redox
91 sensitive element, manganese, by Koho et al. (2015). Studying the interplay between
92 benthic foraminiferal habitat preference and incorporation of redox-sensitive trace
93 elements is key to verifying such models.

94 Studying manganese bound in foraminiferal shell carbonate lies at the
95 intersection of foraminiferal ecology and early diagenesis in sediments. Manganese is
96 a redox sensitive element and exists as Mn- (hydr)oxides in the presence of oxygen. As
97 oxygen concentrations in the sediment decreases due to ongoing organic matter
98 remineralization, Mn-(hydr)oxides are reduced to aqueous Mn^{2+}, (Froelich et al., 1979).
99 Manganese in sediments cycles continuously between solid and aqueous state as a result
100 of upward diffusion of Mn^{2+} and consequent remineralization to Mn-(hydr)oxides.
101 Hence proxy studies must account for both ecological controls, like foraminiferal
102 habitat preference, as well as geochemical controls like oxygen concentrations and
103 organic matter loading (Glock et al., 2012; Groeneveld and Filipsson, 2013; Koho et
104 al., 2015, 2017; McKay et al., 2015; Reichart et al., 2003). Notably, both benthic
105 foraminifera and trace metal geochemistry react to organic matter recycling and bottom

106 water oxygenation (Jorissen et al., 1995). This implies that locations with contrasting
107 conditions, both low and high bottom-water oxygenation as well as low and high
108 productivity, are required for testing. Whereas most of these studies focused on the role
109 of bottom water oxygenation in relatively oxygen poor settings, here we focus on the
110 well-oxygenated western Mediterranean.

111 In this study we combine pore water geochemistry, foraminiferal habitat
112 preference and test geochemistry in an area characterized by well-oxygenated bottom
113 water conditions and average productivity. Results are compared with earlier studies
114 from high productivity regimes and low-oxygen conditions at the sediment-water
115 interface (e.g. Arabian Sea, Koho et al., 2015 and Mediterranean sapropel deposition,
116 Ní Fhlaithearta et al., 2010). Specifically, we investigate the link between manganese
117 incorporation and benthic foraminiferal ecology and compare this to the recently
118 proposed TROXCHEM^3 model (Koho et al., 2015). Four species of living (stained)
119 foraminifera were sampled along a 6-station bathymetric transect in the Gulf of Lions,
120 NW Mediterranean. Individuals were picked from a series of in-sediment depths and
121 analyzed by laser ablation ICP-MS, enabling multiple analyses of single specimens.
122

123 ## 2. Material and methods

124

125 ### 2.1 Study area and sediment sampling

126 Cores were collected with a classical Barnett multicorer (Barnett et al. 1984) at 6
127 stations in the Gulf of Lions (NW Mediterranean) during the August-September 2006
128 BEHEMOTH cruise (Fig. 1, Table 1). The 6 stations describe a bathymetric transect
129 from 350m to 1987m depth. The shallowest site, station F, is bathed in Mediterranean
130 Intermediate Water (MIW). Stations E (552 m) and D (745 m) are positioned at the

transition of MIW and Western Mediterranean Deep Water (WMDW). Stations C (980 m), B (1488 m) and A (1987 m) are bathed by the WMDW. Bottom water temperature is stable through the part of the water column studied here (~13.1°C) (Xavier Durrieu de Madron, pers. com.). Salinity ranges between 38.4 and 38.5. The multicorer allowed sampling of the first decimeters of the sediment, the overlying bottom waters, and an undisturbed sediment-water interface. Cores were sliced for foraminiferal studies with a 0.5-cm resolution down to 4 cm, followed by 1 cm slices down to 10 cm depth. Sediments were put in an ethanol-Rose Bengal mixture (95% ethanol with 1g/l Rose Bengal), in order to identify living (stained) specimens. For more detailed information about methods, please consult Fontanier et al., (2008).

2.2 Pore water geochemistry

Sediment sampling for pore water extraction was carried out under an inert atmosphere (N_2). Hereafter, samples were centrifuged at 3500 rpm for 20 min. The supernatant was filtered and acidified (HNO_3 *s.p.*) for analyzing dissolved metals. Dissolved Mn concentrations were determined with flame atomic absorption spectrometry (Perkin Elmer AA 300). Precision for this method is ± 5%. A pore water subsample was also analyzed for Mn using ICP-MS (Agilent 7500 Series). Relative precision for this method is 3%. Total alkalinity of pore water was measured at Utrecht University using an automated titrator (702 SM Titrino, Metrohm) making Gran plots. Dissolved Inorganic Carbon (DIC) was measured using a Dissolved Carbon Analyser (Shimadzu, Model TOC-5050A). Carbonate ion concentrations were calculated using the CO2SYS software (version 01.05; Lewis and Wallace, 1998). Analytical uncertainty for the alkalinity is about 10 μeq, relative standard deviation for the DIC analyses is 0.8%.

Oxygen concentration profiles were determined using Clark-type microelectrodes (Unisense©, Denmark). Labile organic matter was derived from the sum of lipids, amino acids and sugars measured in the top cm of sediment; for details, see Fontanier et al., 2008.

2.3 Foraminiferal trace metal geochemistry

Foraminiferal trace element concentrations were determined using two laser ablation ICP-MS systems. Prior to laser ablation, all samples were gently cleaned in methanol (x1) and UHQ water (x4). Between each rinse, the samples were placed in a sonic bath for several seconds to thoroughly clean the tests. Benthic foraminifera from 745 m (station D), 980 m (station C), 1488 m (station B) and 1987 m (station A) were measured at Utrecht University using a deep UV (193nm) ArF excimer laser (Lambda Physik) with GeoLas 200Q optics. Ablation was performed at a pulse repetition rate of 10 Hz, and energy density of 1.4 J/cm^2, with a crater size of 80μm. Ablated particles were measured by a quadrupole ICP-MS (Micromass Platform) equipped with a collision and reaction cell. Such a collision and reaction cell improves carbonate analyses by eliminating interferences on mass 44. Scanned masses included ^{24}Mg, ^{26}Mg, ^{27}Al, ^{42}Ca, ^{43}Ca, ^{55}Mn, ^{88}Sr, ^{137}Ba, ^{138}Ba, ^{208}Pb. Benthic foraminifera from stations F (350 m) and E (552 m) were analyzed at ETH-Zurich (due to laboratory renovations at Utrecht University). The laser type and ablation parameters were identical to those detailed above. The ablated particles were measured using a quadrupole ICP-MS (ELAN 6100 DRC, Perkin-Elmer). In both cases, calibration was performed using an international standard (NIST610) with Ca as an internal standard (Jochum et al. 2011). The same masses as measured in Utrecht were monitored, in addition to ^{7}Li, ^{23}Na, ^{47}Ti, ^{60}Ni, ^{61}Ni and ^{89}Y. Inter-laboratory compatibility was monitored using a matrix-matched

calcite standard. For Mn this standard showed a precission better than 3% over all analyses, at ETH and UU, and with an offset of less than 5% from an off line determined (solution ICP-AES) concentration analyzing discrete sub-samples. The matrix matched standard is routinely included in the analyses and has been monitored since 2010 (Duenas Bohorquez et al., 2011).

Analytical error (equivalent to 1 sigma), based on repeated measurement of an external standard, was <5% for reported elements. Each laser ablation measurement was screened for contamination by monitoring Al and Pb. On encountering surface contamination, the data integration interval was adjusted to exclude any Al or Pb enrichment. Cross-plots between Al and Pb versus Mn showed that they are unrelated, confirming accuracy of the integrations.

During the laser ablation analyses the different trace elements were monitored with respect to time, thus representing a cross section of the test wall. This allows not only quantification of the different trace metals of interest, but also to observe variability within individual tests. Each species has a distinct test-wall thickness, permitting the study of intra-test variability. A typical ablation profile for *H. elegans* is shown in Fig. 2.

2.4 Analyses of manganese in foraminiferal tests

Contamination and presence of secondary Mn-rich coatings on benthic foraminiferal tests has been a longstanding challenge in trace metal analyses of benthic foraminifera (Boyle 1983, Lea and Boyle 1989). In this study the trace metal data are based exclusively on living (Rose Bengal stained) foraminifera, which effectively rules out the impact of Mn-rich coatings on trace metal concentrations. At the time of sampling, the collected tests were still enveloped by foraminiferal cytoplasm,

206 preventing the formation of extraneous inorganic precipitates. Although benthic
207 foraminifera live within the sediment, their test is physically separated from the
208 environment as they are enveloped in an organic sheath (Ní Fhlaithearta et al., 2013).
209 In case a recently deceased foraminifer was mistakenly analyzed (still with sufficient
210 protoplasm to stain with Rose Bengal) the Mn oxide would not only have had limited
211 time to develop, but it would also show up as a Mn spike at the start of a laser ablation
212 profile. The ablation profiles confirm that no Mn-rich phases are present at the test
213 surfaces (Fig. 2).
214 Comparing LA-ICP-MS data with traditional solution analyses for foraminiferal
215 Mg/Ca values showed that data are directly comparable (Rosenthal et al., 2011). Also
216 for trace metals such as Ni^{2+}, Cu^{2+} and Mn^{2+}, cross-calibration of LA-ICP-MS and
217 micro-XRF shows those analytical results are robust (Munsel et al., 2010).
218

219 ## 2.5 Benthic foraminiferal Mn/Ca

220 Manganese incorporation in benthic foraminiferal test carbonate was analyzed from 4
221 different species (*Hoeglundina elegans, Melonis barleeanus, Uvigerina mediterranea,*
222 *Uvigerina peregrina*), from 6 coring sites, for up to 9 depths in the sediment. Sample
223 coverage for all stations is described in Table 2. Descriptive statistics are presented in
224 Table 3.
225 From the largest taxon, *Uvigerina mediterranea*, 3-4 analyses were routinely carried
226 out per test, and no trend in Mn/Ca values was seen in consecutive growth stages. From
227 the other species two analyses were performed per test. The resolution of the ablation
228 profiles themselves does not allow quantifying changes in trace metals within the test
229 wall. Still, comparing the data within individual ablation profiles shows that the
230 intratest variability is generally limited for Mn (Table 4). As the ablation profiles target

231 one chamber mostly, this does not include the full potential range. Comparing different
232 ablation profiles between chambers in a single shell would circumvent this, but this data
233 is somewhat limited.
234 Boxplots are used to describe the range of Mn/Ca values and how the distribution,
235 median, average and skewness compares between species. All ICP-MS measurements
236 are included, and as such represent both intra- and inter-individual variation.
237

238 # 3. Results

239 ## 3.1 Pore water data

240 Pore water dissolved manganese (Mn^{2+}) concentrations were measured at all six
241 stations. Manganese concentrations increase below the oxygen penetration depth at
242 stations C and D (Fig. 3), with the highest in-sediment Mn^{2+} concentrations reached at
243 station D. At stations E and F manganese concentrations remain low after crossing the
244 oxygen penetration depth. At stations A and B the oxygen penetration depth and
245 MnO_2/Mn^{2+} redox boundary are deeper than 10 cm's. Dissolved inorganic carbon (DIC)
246 and total alkalinity (TA), were measured at stations E, C and B (Fig. 4). At stations D,
247 C and E, DIC concentrations in the top 10 cm have a similar range (2350-2700
248 μmol/kg). The DIC profile at station B has a narrower range, ranging from 2400-2550
249 μmol/kg. Total alkalinity values range from 3242 μmol/kg at station E to a minimum
250 of 2774 at station B. Carbonate ion concentrations [CO_3^{2-}] were derived based on TA
251 and DIC values. The [CO_3^{2-}] profiles were relatively similar (Fig. 4) for stations E and
252 C and B. Values for all three stations ranged from a maximum of 419 μmol/kg at station
253 E to a minimum of 192 μmol/kg at station C (Fig. 4).

3.2 Mn/Ca data

3.2.1 Intra-individual variability

For most species some Mn/Ca analyses were below detection limit, except for *M. barleeanus,* which contained measurable quantities of Mn in all shells analyzed. This was most evident for *H. elegans*, where all but three Mn/Ca measurements were below detection limit (dl). *Uvigerina peregrina* had a wider range of Mn/Ca values than *U. mediterranea*. *Melonis barleeanus* exhibited the largest range of Mn/Ca values of the four studied species (Fig. 5). For all species, except *H. elegans,* values are somewhat skewed towards higher values.

3.2.3 Foraminiferal Mn/Ca variation across a depth transect

A trend of decreasing manganese incorporation with increasing water depth (350-1987 m) is most clearly visible in *M. barleeanus* (Fig. 6), except that the maximum values are observed at station E at 552 m. *Melonis barleeanus* shows the highest Mn/Ca values and the largest Mn/Ca variability. Station E registers the broadest Mn/Ca variability, which decreases with increasing water depth. *U. peregrina* also exhibits the largest variability in Mn/Ca values at station E. For *U. peregrina*, Mn^{2+} incorporation decreases from 350 m to 1987 m, except for station D (745 m), where Mn/Ca values (between the 10 – 90th percentile) are approximately equivalent to those at station A (350 m; Fig. 6). For *U. mediterranea* a trend of decreasing Mn incorporation with increasing depth is found in specimens of *U. mediterranea* from the sediments at 552, 745 and 980 m. The highest values are reached at the shallowest station (350 m). Station E is also marked by the highest minimum Mn/Ca values for *U. mediterranea*. At station A only two *U. mediterranea* measurements are above the detection limit. *Hoeglundina elegans* shells from three stations (350 m, 1488 m and 1987 m) were analyzed, however, all but three

279 measurements were below detection limit (Fig. 6). These slightly elevated values were
280 recorded at the shallowest station (station F). These Mn/Ca values are still very low
281 compared to ranges in Mn/Ca values observed for the other species (Fig. 6).

282 Variability in Mn/Ca increases together with the overall Mn/Ca concentration
283 within benthic foraminiferal species (Table 4). This suggests that even at those stations
284 and depth levels where the highest Mn concentrations are recorded, individuals with
285 relatively low amounts of Mn in their calcitic test were found. Comparing relative
286 standard deviations, as a measure for the inter-specimen variability, for the different
287 stations and species suggests that with increasing Mn concentration for *M. barleeanus*
288 and *U. mediterranea* variability increases, whereas for *U. peregrina* it decreases.

289

290 **3.2.4 In-sediment variation**

291 For most species Mn/Ca values are more or less constant with in-sediment depth (Fig.
292 3). However, *M. barleeanus* shows increasing Mn/Ca values with in-sediment depth.
293 This is most apparent at the shallowest station (station F - 350 m) (Fig. 3d).

294

295 # 4. Discussion

296

297 Incorporation of Mn in benthic foraminiferal carbonate depends both on foraminiferal
298 ecology and early diagenesis in sediments. Although other factors such as temperature,
299 sea water carbonate chemistry, growth rate etc., might also affect the uptake of Mn in
300 the shell carbonate (Koho et al., 2017), these effects are most likely several orders of
301 magnitude smaller compared to the large range in dissolved Mn in pore water. Since
302 pore water Mn is the dominant factor controlling Mn incorporation, studies must
303 account for ecological controls, like foraminiferal depth habitat preference, as well as

for geochemical controls like oxygen concentrations and organic matter fluxes (Koho et al., 2015; De Lange, 1986; Reichart et al., 2003). The fact that this study was based on living foraminifera circumvents potential complications due to Mn-rich coatings. Such coatings would likely not affect the aragonitic shell of *H. elegans* (Ní Fhlaithearta et al., 2010), but might interfere when analyzing fossil calcite shells. Still, a spatially resolved analytical technnique like LA-ICP-MS allows detecting such coatings also in fossil specimens.

4.1 Impact of redox conditions and foraminiferal habitat preference on Mn incorporation

In general, flux of organic matter arriving at the sea floor decreases with increasing water depth, due to ongoing degradation during settling (Arndt et al., 2013 and references theirein). Consequently, redox boundaries within the sediment generally also deepen as a function of water depth, as oxygen consumption in the sediment decreases. Such a fundamental organic matter-depth relation is in line with the much deeper oxygen penetration depths at stations A and B compared to the more shallow stations. At station F the relative shallow oxygen penetration depth observed is in line with its' relative shallow water depth, although the organic matter which arrives here at the seafloor apparently undergoes winnowing (Fontanier et al., 2008). The organic matter along the transect studied is concentrated at a so-called depocenter, which largely coincides with the depths of stations C and D (Fontanier et al., 2008). As bottom waters at all stations are well oxygenated, organic matter concentration can be considered the main control for redox conditions at stations F-A, with the amount of organic matter arriving at the seabed being regulated by water depth and sedimentary processes, such as focusing versus winnowing.

329 At stations C, D and F, the oxygen penetration depth and the Mn^{2+} redox
330 boundaries are at the same depth, as expected. Station F shows the shallowest OPD of
331 all stations, although the organic matter concentration is relatively low. One explanation
332 for this observation is that a lower porosity at F (56% versus 76% and 79 % at stations
333 D and E, respectively) impedes oxygen diffusion through the sediment. Alternatively,
334 the pore water profile reflects an earlier organic matter deposition event, with this
335 organic matter being largely consumed at the time of sampling. The pore water profiles
336 require more time to re-equilibrate to the new conditions (Burdige and Gieskes, 1983).
337 At station E there is a mismatch between oxygen penetration depth and the Mn^{2+} redox
338 boundary as the Mn^{2+} redox boundary is considerably deeper than the OPD. Although
339 this is in line with the observed higher bioirrigation at this station (Fontanier et al.,
340 2008), this might reflect non-equilibrium conditions as well.
341 The vertical distribution of benthic foraminiferal species varies between
342 stations, in accordance with organic matter concentrations and redox zonation, which
343 is consistent with the TROX model (Jorissen et al., 1995; Fontanier et al., 2008). In
344 case of a shallower redox zone, infaunal benthic foraminifera biomineralize in contact
345 with Mn-enriched pore water, with highest dissolved manganese concentrations
346 occurring just below the oxygen penetration depth at all stations, except for station E
347 (552 m). This is in contrast to low bottom-water oxygen environments often studied in
348 the context of proxy development studies, where pore water Mn^{2+} is released from the
349 pore water (Koho et al., 2015, 2017; Mangini et al., 2001).
350 The species studied here cover the range of shallow-infauna to intermediate-
351 infauna niches. Both *Uvigerina mediterranea* and M. barleeanus were in the Gulf of
352 Lyons found to occupy shallow to intermediate infaunal habitat, with *U. peregrina*
353 having a somewhat shallower infaunal habitat (Fonatnier et al., 2008). *Hoeglundina*

354 *elegans*, a typically shallow infaunal species, is often found close to the sediment-water
355 interface (Jorissen et al., 1998; Schönfeld 2001; Fontanier et al., 2002; Fontanier et al.,
356 2008) and contains the lowest concentration of Mn in its test. Only at the shallowest
357 station (350 m) three specimens of *H. elegans* show concentrations above the detection
358 level, with values still low compared to the values observed for the other species (Fig.
359 6). In the Bay of Biscay Reichart et al. (2003) also suggested that elevated Mn
360 concentrations in *H. elegans* were confined to stations with oxygen depleted bottom
361 waters and/or with a shallow oxygen penetration depth. *Uvigerina mediterranea* and
362 *Uvigerina peregrina* are also classed as shallow-infaunal species; they are typically
363 found within the top few centimeters of the sediment column (Fontanier et al. 2002,
364 Fontanier et al. 2008). The calculated average living depth (ALD_{10}) as calculated in
365 Fontanier et al. (2008) is consistently shallower than the ALD_{10} for *U. mediterranea*.
366 This is at odds with previous reports suggesting *U. peregrina* has a slightly deeper
367 microhabitat than *U. mediterranea* (Fontanier et al. 2002; 2006). That *U. peregrina* has
368 a deeper microhabitat is further supported by the usual distinct $\partial^{13}C$ offset in *U.*
369 *peregrina,* which is more depleted compared to *U. mediterranea* (Schmiedl et al., 2004;
370 Fontanier et al, 2002, 2006). The higher Mn/Ca values observed here for *U. peregrina*
371 (Figure 6) supports the idea that it calcifies somewhat deeper in the sediment compared
372 to *U. mediterranea*. Alternatively, *U. peregrina* may migrate downwards within
373 burrows to track food resources, recording redox steepness (Loubere et al., 1995). This
374 could highlight a disparity between the assumed living depth (the depth interval of
375 recovery) and biomineralization depth of foraminifera. Still, this would also result in a
376 higher variability of Mn/Ca values at higher Mn/Ca levels, which is not observed.
377 Hence, more likely the observed disparity between the geochemical signals
378 incorporated into foraminiferal calcite and depth of recovery in *U. peregrina* reflects

379 opportunistic behaviour, with calcification at a shallower in-sediment depth in response
380 to more favourable conditions after e.g. seasonal peaks in organic matter fluxes
381 (Accornero et al., 2003), when the OPD is close to the sediment water interface.

382 *Melonis barleeanus*, generally considered an intermediate-infaunal species
383 (Fontanier et al., 2002, 2008), contains the highest concentrations of Mn in its test,
384 which is in line with the deepest habitat of the species studied here. Manganese
385 incorporation in this species increases with increasing labile organic matter (Fig. 7a).

386 In summary, the habitat preference of the benthic foraminiferal species studied
387 here is reflected in the Mn/Ca values recorded in their tests. This is in contrast with
388 other results showing lower Mn/Ca values in foraminiferal tests with shallower redox
389 fronts (Koho et al., 2015). This, however, critically depends on the Mn being released
390 to the water column, which only occurs when the bottom waters are disoxic. In case of
391 a seasonal organic matter deposition event, an increase of Mn concentration in
392 foraminiferal test carbonate would initially occur in the deeper and ultimately also in
393 the more shallow calcifying foraminifera. This is in line with the conceptual
394 TROXCHEM[3] model, with the conditions studied here falling within the first stage of
395 the temporal succession considered in the model. Bottom water remains well
396 oxygenated (O_2 concentrations at the study area: 199-219 μmol/l (Fontanier et al.,
397 2008)) and organic matter loading is controlling Mn^{2+} concentrations in the sediment.
398 To what extend species are high in Mn/Ca depends on living depth and opportunistic
399 behavior.

400 At a given location, a benthic foraminiferal species' depth preference or
401 biomineralization depth, is reflected in its average Mn/Ca value (Fig. 5). The trend
402 across a depth transect shows a strong correlation to labile organic matter
403 concentrations in the surface sediments (Fig. 7). The strong correlation between labile

404 organic matter (i.e. sedimentary lipid content) and Mn incorporation in shallow and
405 intermediate infaunal species *U. mediterranea* ($R^2 = 0.80$ ($p < 0.05$) suggests that test
406 Mn has potential as a proxy for detecting past labile organic matter fluxes. Noteably,
407 *M. barleeanus* has a very strong correlation (0.81), though this correlation lacks
408 statistical significance ($p > 0.05$). In contrast, *U. peregrina* shows a correlation
409 coefficient of only 0.45 (R^2) between test Mn and labile organic matter. *Uvigerina*
410 *peregrina* is reported to respond opportunistically to the concentration and quality of
411 organic matter produced during bloom events (Fontanier et al., 2003; Koho et al., 2008;
412 Barras et al., 2010). This response is in the form of increased reproduction and growth.
413 Perhaps *U. peregrina* calcifies preferentially at shallower depths and therefore does not
414 capture the full Mn^{2+} gradient.

415 At low oxygen concentrations Mn is released through the reduction of
416 manganese (oxy)hydroxides. Here we show an increase in Mn/Ca incorporation in
417 several species, from shallow to intermediate-depth infaunal habitats, as a function of
418 oxygen penetration depth. Such a correlation agrees with studies by Ní Fhlaithearta et
419 al. (2010) and McKay et al. (2015) from a down core record of $Mn/Ca_{H. elegans}$ during the
420 formation of sapropel (S1) in the Eastern Mediterranean and a paleoproductivity study
421 of an upwelling system in the NE Atlantic, respectively. Here, a comparison of Mn
422 (oxy)hydroxides in the sediment and foraminiferal Mn^{2+} showed that Mn^{2+}
423 incorporation in an epifaunal to shallow infaunal species was higher during times of
424 enhanced Mn^{2+} remobilization and hence higher pore water Mn^{2+}. Such a correlation,
425 however, requires that the bottom waters remain somewhat oxygenated to retain the
426 dissolved Mn^{2+} in the pore water. With disoxic bottom waters Mn^{2+} escapes the
427 porewater and foraminiferal Mn/Ca values decrease (Koho et al., 2015). However, with
428 high organic matter deposition, which might be concentrated in events, also

429 foraminiferal species living at or close to the sediment water interface may show
430 elevated Mn concentrations.

431 In addition to the here observed changes, biomineralization could affect Mn^{2+}
432 incorporation. In a controlled laboratory study by Munsel et al (2010) Mn
433 incorporation in *Ammonia tepida* increased with increasing Mn^{2+} concentrations in the
434 culture water and the partition coefficient was well above 1. The lack of an
435 appreciable discrimination argues against a major biomineralization impact on Mn^{2+}
436 partitioning. Recently Barras et al. (2018), also using controlled growth experiments,
437 showed, however, that Mn partitioning in *B. marginata* differs from that in *A. tepida*,
438 with that in B. marginat being close to one and that of A. tepida being 4 times lower.
439 Inter-specific differences are considerable and hence an impact of biomineralization
440 on Mn incorporation can not be disregarded .

441 In summary, Mn incorporation seems primarily controlled by pore water
442 conditions in close proximity to the test, biomineralization and with a secondary
443 control determined by the ability of a foraminifer to seasonally calcify and migrate
444 within the sediment.

445
446 **4.2 Pore water Mn dynamics and foraminiferal migration within the sediment**

447 Manganese is incorporated in foraminiferal carbonate with a partition coefficient (D)
448 close to 1 or somewhat lower (Munsel et al., 2010; Barras et al., 2018). We calculated
449 Mn partition coefficients for *U. mediterranea*, *U. peregrina* and *M. barleeanus* at
450 stations E, C and B (Table 6) based on average Mn/Ca_{foram} and average $Mn/Ca_{pore\ water}$
451 values found above the Mn^{2+}-MnO(H) redox boundary. Calculated D_{Mn} agrees with the
452 previously reported D_{Mn} by Munsel et al., (2010), with values varying between ~1-2 for
453 *U. mediterranea* and *U. peregrina*. The Mn partition coefficient for *Melonis barleeanus*
454 ranges from ~4-7. The partition coefficient for this species most likely reflects its

455 capacity to calcify under dysoxic conditions, close to or even below the oxygen
456 penetration depth. Still, this calculation is based on two assumptions: (1) the depth
457 foraminifera are recovered from during sampling corresponds with the average depth
458 of calcification and, (2) variation in pore water is limited. Establishing species specific
459 Mn partitioning coefficients using culture experiments might, however, be needed for
460 unlocking the full potential of this proxy (Barras et al., 2018).

461 A foraminifer calcifying within a steep Mn^{2+} gradient is exposed to a higher
462 range of Mn^{2+} concentrations (over a fixed depth interval) compared to specimens living
463 along a more gradual Mn^{2+} concentration gradient. Since foraminifera can migrate
464 through the sediment as a response to food availability and oxygen concentrations (Alve
465 and Bernhard 1995; Gross, 2000), not only the slope of the Mn gradient, but also the
466 in-sediment depth range (microhabitat) of the foraminifer in relation to the Mn redox
467 boundary, should be considered (Fig. 8). Although the analyses of foraminiferal test
468 Mn/Ca is challenging, which adds to the inter-specimen variability, we observe
469 systematic differences between species in Mn/Ca variability. A shallow-infauna
470 species, with a limited in-sediment range, would be expected to exhibit lower variability
471 than an intermediate- infauna species, which possibly migrates considerably in depth.
472 This is exemplified at station F (350 m) where we note an increase in foraminiferal test
473 Mn/Ca variability at 2 cm depth, consistent with the oxygen penetration depth at that
474 station (Fig. 3). Moreover, the variability in Mn/Ca values increases towards higher
475 Mn/Ca values. This is in line with the depth habitat of *M. barleeanus* being consistently
476 deeper and this species traveling more actively through the redox zones than *U.*
477 *mediterranea* or *U. peregrina*. Nitrate respiration could be mechanism allowing this
478 dynamic behaviour by *M. barleeanus* in the intermediate depth habitat. However, Pina-
479 Ochao et al. (2010), studying denitrification in foraminifera, reports nitrate storage in

480 all three species mentioned here. Notably, nitrate storage in *M. barleeanus* is lower than
481 *U. mediterranea* and *U. peregrina*. Alternatively *M. barleeanus* thrives in habitats with
482 varying oxygenation and hence also varying Mn levels, whereas the stable but high
483 Mn/Ca values in the Uvigerinids are related to their opportunistic behaviour.

484 With a redox-sensitive element such as Mn, in a dynamic geochemical
485 environment, it is not surprising that foraminifera exhibit high inter-individual
486 variability in their Mn/Ca incorporation. Benthic foraminifera reside in a 3D
487 geochemical mosaic, as reflected by a large spread of Mn values, in addition to
488 undergoing substantial temporal variability. Still, using Mn/Ca as a potential proxy for
489 redox conditions or primary productivity seems promising, as established ecological
490 characteristics of species are reflected by differences in Mn incorporation. Apparently
491 the large variability on both spatial and temporal scales averages out, making Mn into
492 a promising proxy for paleo-redox and organic matter flux.

493

494 **5. Conclusion**

495 This study investigates the link between benthic foraminiferal habitat preferences and
496 manganese incorporation in their tests. Manganese incorporation increases with
497 bottom-arriving labile organic matter content, driven by enhanced oxygen demand.
498 This results in a more shallow oxygen penetration depth with immediately below it
499 enhanced dissolved Mn levels. Shallow infaunal species calcify under lower
500 concentrations of Mn compared to intermediate infauna, in line with their depth
501 preference. Their depth habitat is related to in-sediment changes in redox conditions.
502 However, these distribution not necessarily vary synchronous with changes in redox
503 zonation as illustrated by the Mn/Ca variability in their tests (Fig. 8). The latter reflects
504 the Mn/Ca porewater composition, which itself is directly related to reactive organic

matter concentration and redox conditions. The foraminiferal Mn/Ca ratio and inter-specimen variability, therefore, provides information on past Mn cycling within the sediment. Consequently, foraminiferal Mn/Ca ratio is a potential proxy for bottom-water oxygenation and organic matter fluxes.

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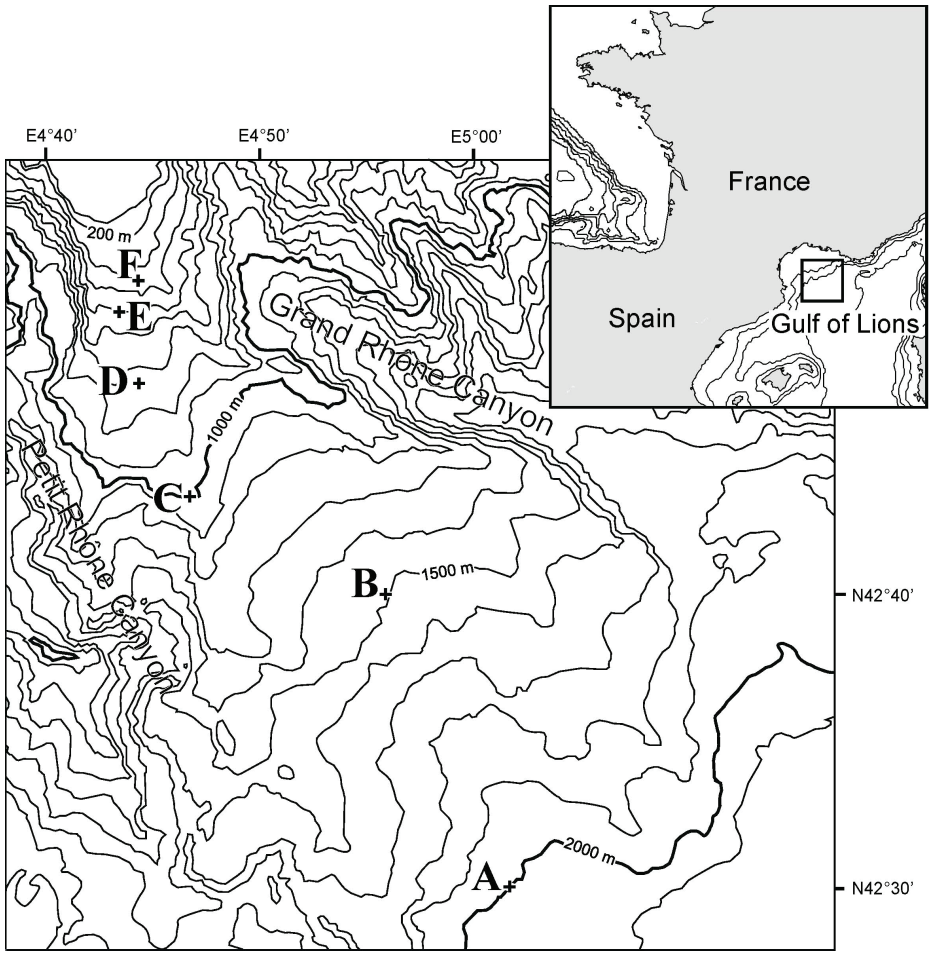

Figure 1. Location map showing sampling stations and bathymetry.

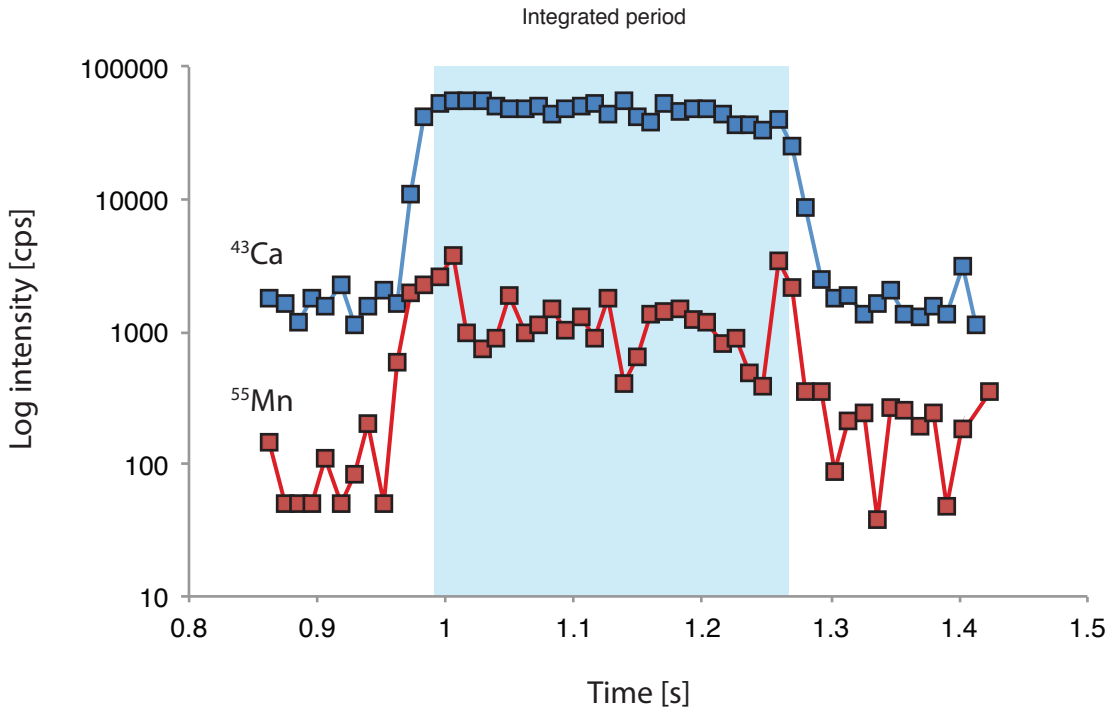

Figure 2. Example of a laser ablation profile, signal log intensity counts per second [cps] through time. The integrated signal is shaded.

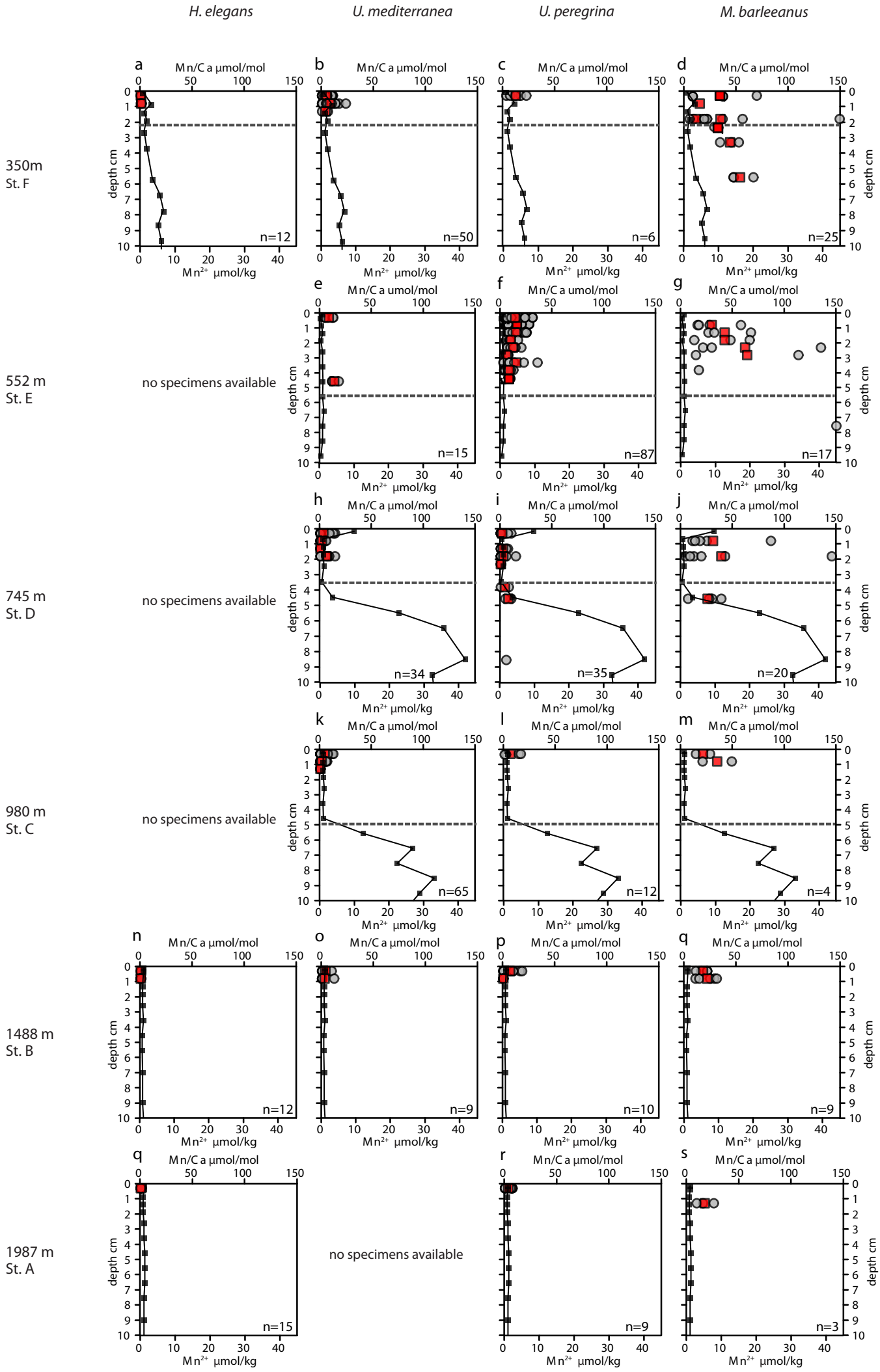

Figure 3. Plots of Mn/Ca (µmol/mol) measured in living (stained) Hoeglundina elegans, Uvigerina mediterranea, Uvigerina peregrina and Melonis barleeanus. Individual analyses are plotted (grey circles) alongside average values for a given depth in the sediment (red squares). Porewater Mn2+ (µmol/kg) profiles (black line) are plotted for all stations. The dashed grey line indicates the oxygen penetration depth (OPD).

Figure 4.

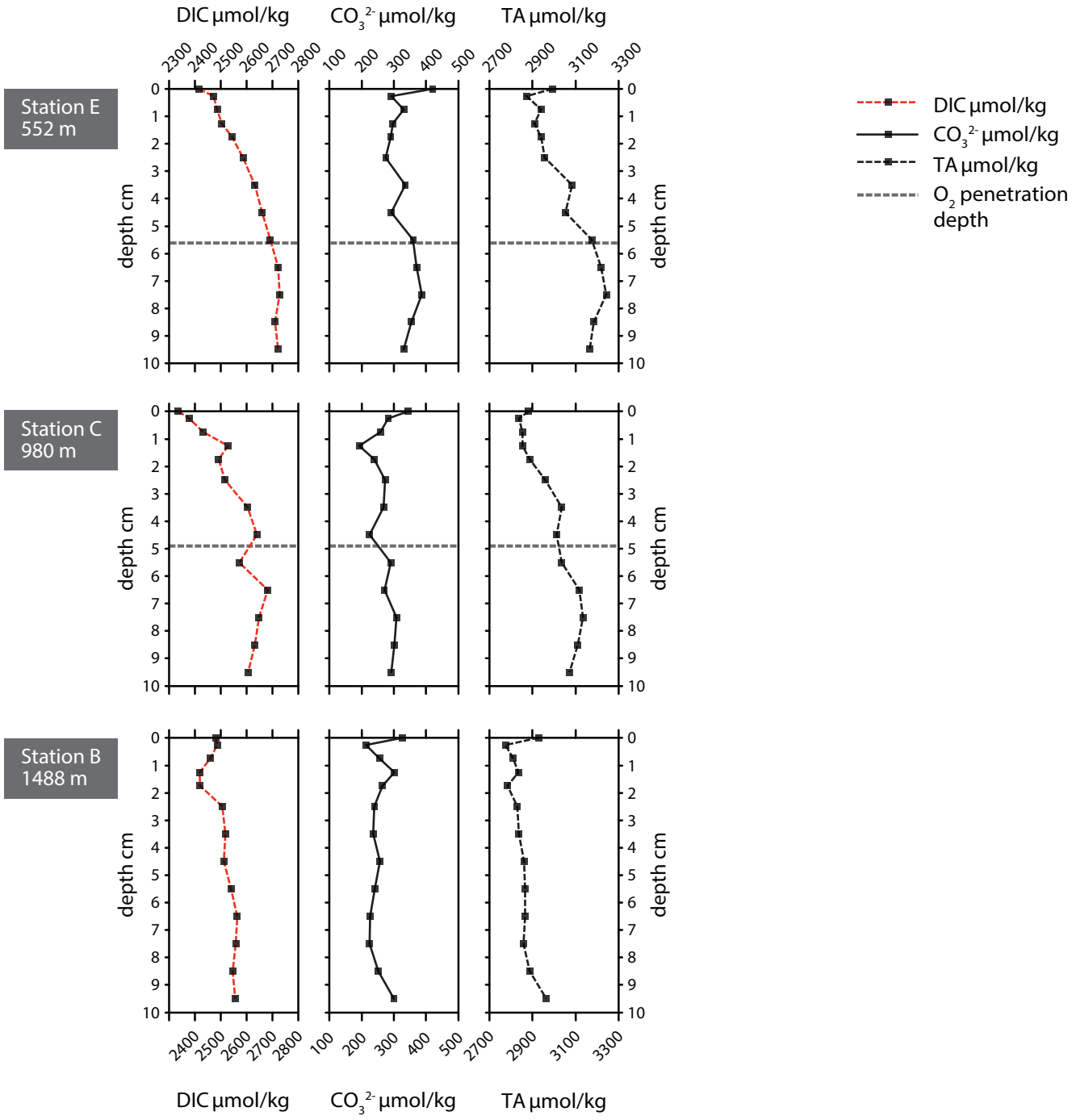

Figure 4. Carbonate chemistry parameters for stations E, C and B. A) Dissolved inorganic carbon (DIC), B) [CO32-] in µmol/kg, C) Total alkalinity (TA) in µmol/kg.

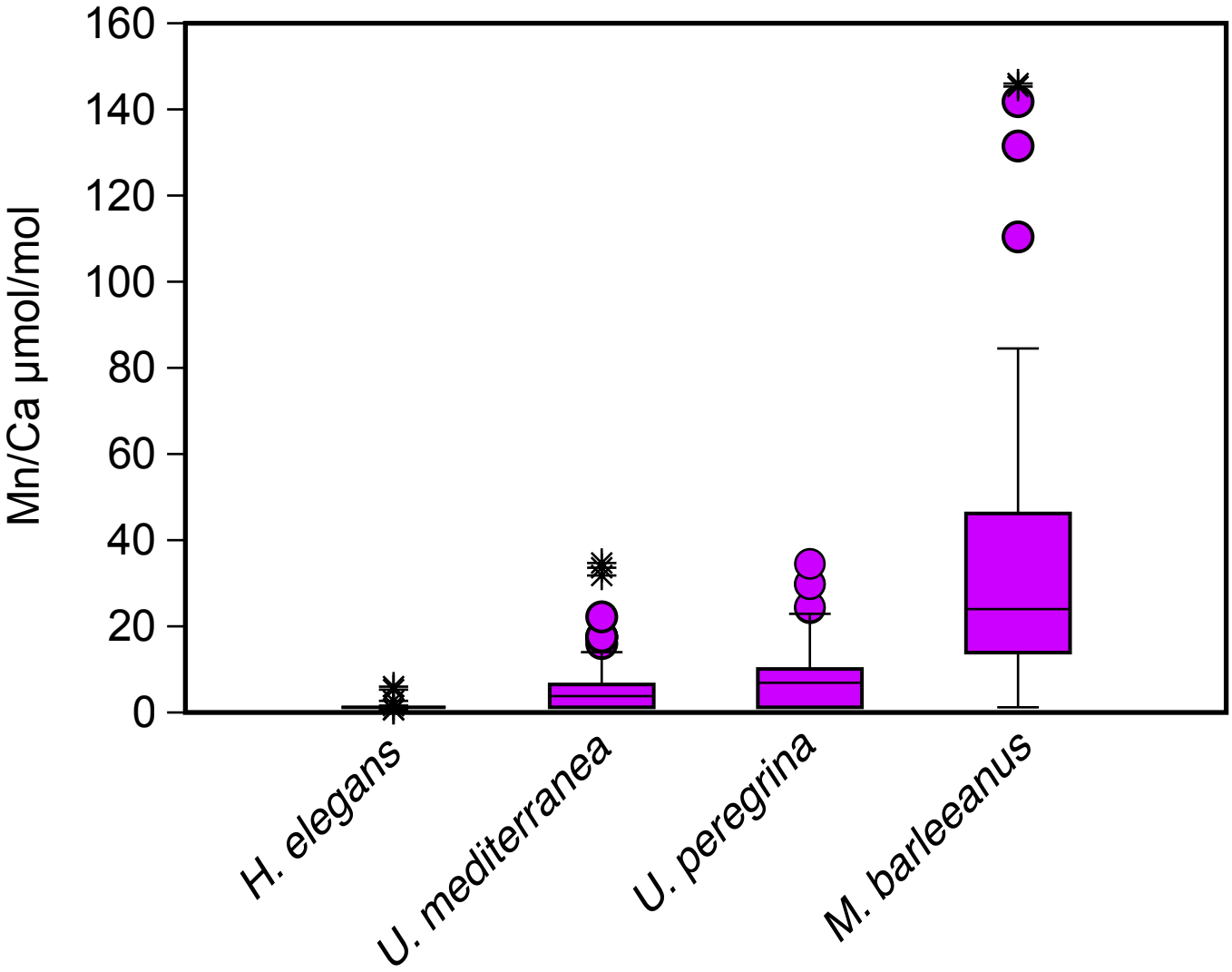

Figure 5. Box plots describing the distribution in Mn/Ca values measured in living (stained) individuals of Hoeglundina elegans, Uvigerina mediterranea, Uvigerina peregrina and Melonis barleeanus. The box represents all values between the 25th and 75th percentile. The dissection line through the box denotes the median. The whiskers are drawn from the top of the box up to the largest data point less than 1.5 times the box height from the box and similarly below the box. Values outside the whiskers are shown as circles, values further than 3 times the box height are denoted as stars.

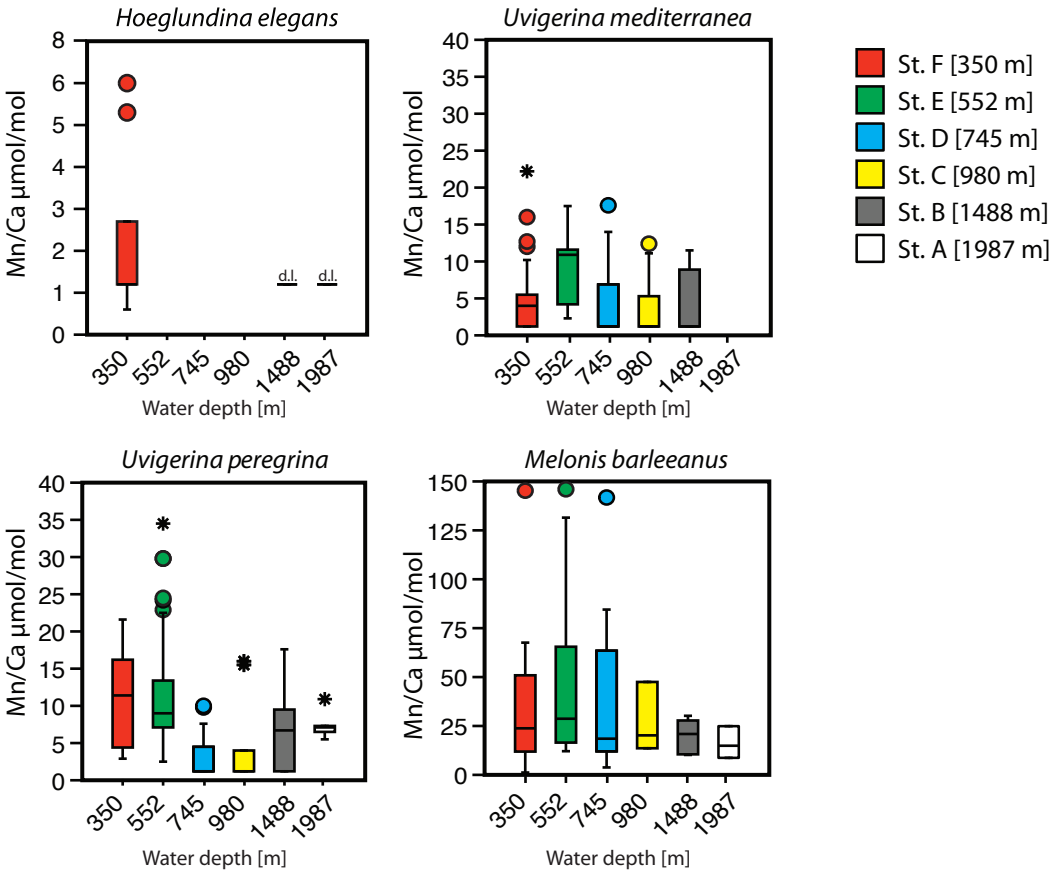

Figure 6. Box plots describing the distribution of Mn/Ca values across a depth transect (350-1987 m) measured in living (stained) individuals of Hoeglundina elegans, Uvigerina mediterranea, Uvigerina peregrina and Melonis barleeanus. Note that the scale of the y-axis varies. The box represents all values between the 25th and 75th percentile with the whiskers extending less than 1.5 times the box height. The dissection line through the box denotes the median. Values outside the whiskers are shown as circles, values further than 3 times the box height are denoted as stars.

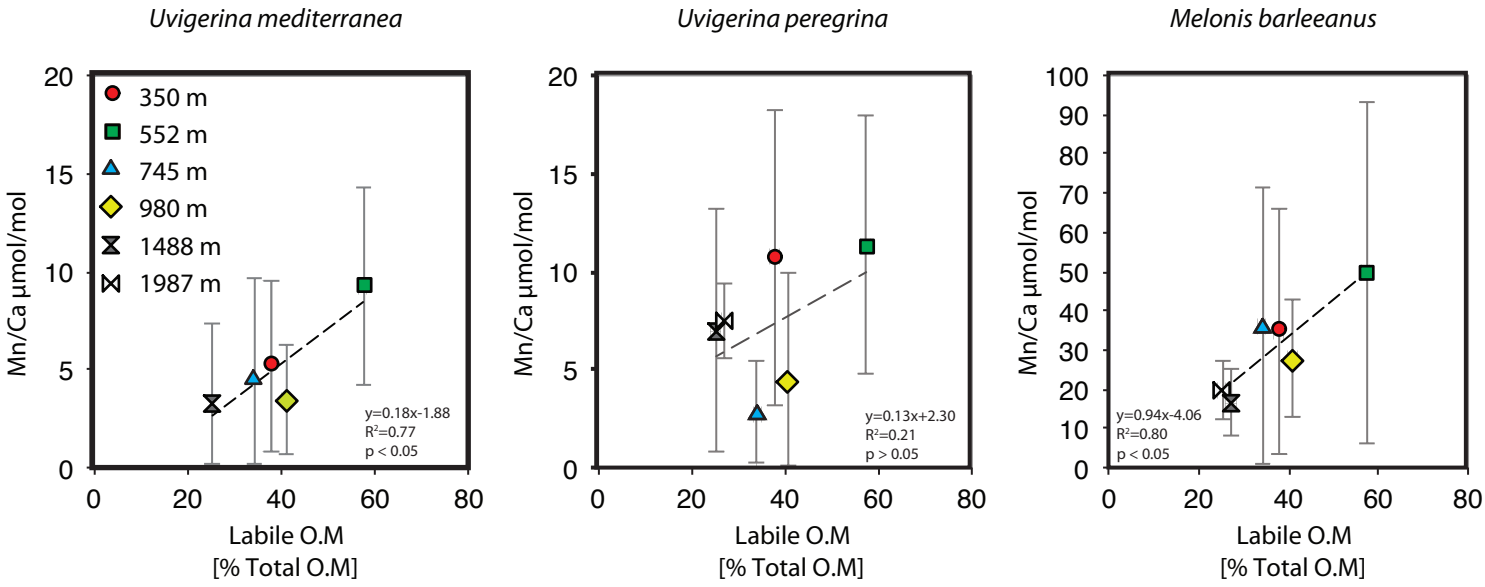

Figure 7. Plots of average Mn/Ca µmol/mol versus labile organic matter [% Total Organic matter].

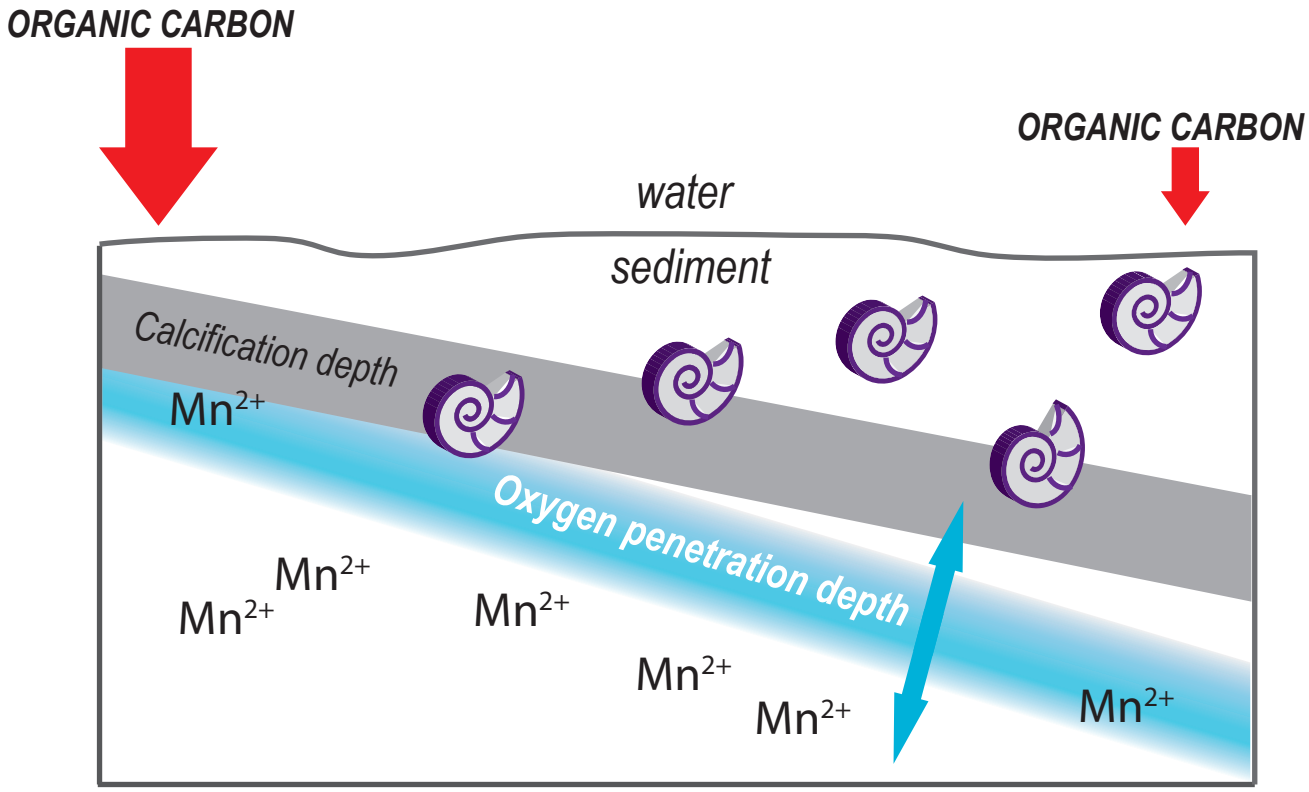

Figure 8. Schematic diagram of a shallow-infaunal and intermediate-infaunal benthic foraminifera and their spatial relationship with the sediment redox boundaries, migration zone, ALD and calcification depth.

Table 1. Water depth, coordinates and bottom water physio-chemical parameters: Temperature (°C), salinity, and oxygen penetration depth mm) for six stations F-A. (* Xavier Durrieu de Madron, Pers. Comm.)

Station	Depth (m)	Latitude (N)	Longitude (E)	Bottom water temperature* (°C)	Bottom water salinity *	Oxygen penetration depth (mm)
F	350	42°52'32	4°42'43	13.2	~38.5	20.5 ±3.3
E	552	42°48'78	4°43'21	13.2	~38.5	57.2 ±4.5
D	745	42°46'66	4°43'91	13.1	~38.5	36.5 ±1.6
C	980	42°43'18	4°46'58	13.1	~38.48	50.7 ±6.3
B	1488	42°38'83	4°56'03	13.1	~38.46	141.5 ±0.0
A	1987	42°28'25	5°00'61	13.1	~38.46	197.0 ±11.0

Table 2. Number of LA-ICP-MS analyses per benthic foraminifera species per sample per station.

Station	**Depth (m)**	**Sample intervals (cm)**	***Hoeglundina elegans* no. analyses**	***Uvigerina mediterranea* no. analyses**	***Uvigerina peregrina* no. analyses**	***Melonis barleeanus* no. analyses**
F	350	0-0.5	2	18	5	1
		0.5-1	4	13		2
		1-1.5		3		
		1.5-2				10
		2-2.5	1			2
		3-3.5				3
		5-6				3
E	552	0-0.5		5	26	
		0.5-1			9	4
		1-1.5			14	3
		1.5-2			5	3
		2-2.5			7	3
		2.5-3			6	2
		3-3.5			6	
		3.5-4			8	1
		4-5		3		
		7-8				1
D	745	0-0.5		20	13	
		0.5-1		6		5
		1-1.5		3	6	
		1.5-2		7	8	6
		2-2.5			4	
		3.5-4			2	
		4-5			2	4
		8-9			2	
C	980	0-0.5		20		2
		0.5-1		20		2
		1-1.5		4		
B	1488	0-0.5	3	4	10	4
		0.5-1	9	5	3	5
A	1987	0-0.5	15		10	
		1-1.5				3

Table 3. Descriptive statistics (minimum, maximum, mean, median, standard deviation and interval of maximum frequency of total analyses for *H. elegans*, *U. mediterranea*, *U. peregrina* and *M. barleeanus* for Mn/Ca µmol/mol.

Mn/Ca µmol/mol	***H. elegans***	***U. mediterranea***	***U. peregrina***	***M. barleeanus***
Min	dl*	dl*	dl*	3.91
Max	0.69	22.71	35.38	149.50
Mean	0.04	4.03	8.28	37.22
Median	dl*	1.04	7.45	24.76
Std. deviation	0.16	5.03	7.17	35.17
Max. frequency interval	dl-7.50 (100% < 1)	dl-7.50 (80%)	dl-7.50 (53%)	7.5-15 (23%)

Table 4. Relative standard deviation (% RSD) of intra-individual values in Mn/Ca within four species of benthic foraminifera (*H. elegans*, *U. mediterranea*, *U. peregrina* and *M. barleeanus*).

Element	***H. elegans* % RSD**	***U. mediterranea* % RSD**	***U. peregrina* % RSD**	***M. barleeanus* % RSD**
Mn	21	23	20	51

Table 5. Relative standard deviation (% RSD) of inter-individual values in Mn/Ca within four species of benthic foraminifera (*H. elegans*, *U. mediterranea*, *U. peregrina* and *M. barleeanus*).

Element	***H. elegans* % RSD**	***U. mediterranea* % RSD**	***U. peregrina* % RSD**	***M. barleeanus* % RSD**
Mn	400	125	87	97

Table 6. Manganese porewater – carbonate partition coefficient for foraminiferal species *Uvigerina mediterranea*, *Uvigerina peregrina* and *Melonis barleeanus*.

	Partition coefficient (D)[1]		
Station	***U. mediterranea***	***U. peregrina***	***M. barleeanus***
E (552 m)	1.7	1.8	7.0
C (980 m)	1.2	-	5.1
B (1488 m)	2.2	2.3	4.1

[1]Porewater-carbonate partition coefficients were calculated using the average porewater Mn/Ca [µmol/mol] measured above the oxygen penetration depth and the average carbonate Mn/Ca [umol/mol] measured in *U. mediterranea*, *U. peregrina* and *M. barleenanus*, for all specimens recovered above the reported oxygen penetration depth (Fontanier et al., 2008).