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

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17

18 **Abstract**

19 Manganese geochemistry in deep-sea sediments is known to vary greatly over the first

20 few centimeters, which overlaps with the in-sediment depth habitats of several benthic

21 foraminiferal species. Here we investigated manganese incorporation in benthic

22 foraminiferal shell carbonate across a 6-station depth transect in the Gulf of Lions,

23 NW Mediterranean to unravel the impacts of foraminiferal ecology and Mn pore

24 water geochemistry. Over this transect water depth increases from 350 to 1987 m,

25 while temperature (~13˚C) and salinity (~38.5) remained relatively constant.

26 Manganese concentrations in the tests of living (Rose Bengal stained) benthic

27 foraminiferal specimens of *Hoeglundina elegans*, *Melonis barleeanus, Uvigerina*

28 *mediterranea*, *Uvigerina peregrina* were measured using laser ablation inductively

29 coupled mass spectrometry (laser ablation ICP-MS). Pore water manganese

30 concentrations show a decrease from shallow to deeper waters, which corresponds to

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31 a generally decreasing organic matter flux with water depth. Differences in organic

32 matter loading at the sediment water interface affects oxygen penetration depth into

33 the sediment and hence Mn pore water profiles. Mn/Ca values for the investigated

34 foraminiferal species reflect pore water geochemistry and species-specific

35 microhabitat in the sediment. The observed degree of variability within a single

36 species is in–line with know ranges in depth habitat and gradients in redox conditions.

37 Both Mn/Ca ratio and inter-specific variability hence reflect past Mn cycling and

38 related early diagenetic processes within the sediment, making this a potential tool for

39 bottom-water oxygenation and organic-matter fluxes. Dynamics of both in-sediment

40 foraminiferal depth habitats and Mn cycling, however, limit the application of such a

41 proxy to settings with relatively stable environmental conditions.

42

43 **1. Introduction**

44

45 Reconstructing past climate and environmental change largely depends on so-called

46 proxies. These proxies relate measurable variables in the geological record to target

47 parameters, such as e.g. temperature, biological productivity and bottom water

48 oxygenation. The carbonate shells of unicellular protists, foraminifera, are one of the

49 most utilized signal carriers for reconstructing past environments. Both the census

50 data of foraminifera and the geochemical composition of the shells are used in this

51 context. The geochemical composition of the shells is investigated for their stable

52 isotopic composition as well as for their trace and minor element incorporation. Both

53 surface and bottom water conditions are reconstructed this way, using planktonic and

54 benthic foraminiferal species respectively.

55   Most existing calibrations of trace element uptake in foraminiferal test

56 carbonate are based on comparing their composition with bottom water conditions

57 (Elderfield et al., 2006; Nürnberg et al., 1996; Yu and Elderfield, 2007). Many

58 benthic foraminiferal species live, however, within the sediment and precipitate their

59 calcium carbonate test in contact with pore water. As a result, the trace metal

60 composition of pore water exerts a control on the uptake of trace metals in their test.

61 This effectively links benthic foraminiferal microhabitat preference and pore water

62 chemistry. On the one hand, this creates complications when using foraminiferal trace

63 metal ratios for reconstructing bottom water conditions, whereas on the other hand, it

64 offers the possibility to develop proxies of pore water chemistry in the past.

65 Linking foraminiferal test chemistry with pore water chemistry requires in-

66 depth knowledge of, 1) how early diagenesis in sediments affects pore water

67 chemistry, 2) the habitat preference of the foraminiferal species, 3) foraminiferal

68 migration (and calcification) within the uppermost sediment layer. In principle, the

69 chemical composition of living (stained) benthic foraminifera will reflect all these

70 processes.

71 For many elements an important inter-specific difference in uptake of trace

72 metals has been observed (Hintz et al., 2006; Wit et al., 2012), a so-called vital effect.

73 This implies that in addition to ecology and pore water geochemistry, trace metal

74 partitioning also needs to be taken into consideration. This requires a comparative

75 study between locations where all three of these aspects have been quantified.

76 Reconstructing past pore water trace metal profiles is important since it

77 provides valuable information on organic carbon degradation and recycling of

78 nutrients at the seafloor (Van Cappellen and Wang, 1996; De Lange, 1986). Such

79 diagenetically controlled trace metal profiles are used in quantitative models

80 constraining oceanic carbon fluxes and burial (Wang and Van Cappellen, 1996).

81 Knowledge of such profiles in the past could thus help to reconstruct past carbon

82 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

86 have a wider distribution, thriving under variable conditions and consequently occupy

87 a 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

90 be related, such as recently proposed in a conceptual (TROXCHEM[3]) model for the

91 redox sensitive element, manganese, by Koho et al. (2015). Studying the interplay

92 between benthic foraminiferal habitat preference and incorporation of redox-sensitive

93 trace 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.

97 As 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.,

99 1979). Manganese in sediments cycles continuously between solid and aqueous state

100 as a result of upward diffusion of Mn^{2+} and consequent remineralization to Mn-

101 (hydr)oxides. Hence proxy studies must account for both ecological controls, like

102 foraminiferal habitat preference, as well as geochemical controls like oxygen

103 concentrations and organic matter loading (Glock et al., 2012; Groeneveld and

104 Filipsson, 2013; Koho et al., 2015, 2017; McKay et al., 2015; Reichart et al., 2003).

105 Notably, both benthic foraminifera and trace metal geochemistry react to organic

106   matter recycling and bottom water oxygenation (Jorissen et al., 1995). This implies

107   that locations with contrasting conditions, both low and high bottom-water

108   oxygenation as well as low and high productivity, are required for testing. Whereas

109   most of these studies focused on the role of bottom water oxygenation in relatively

110   oxygen poor settings, here we focus on the 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

131   transition of MIW and Western Mediterranean Deep Water (WMDW). Stations C

132   (980 m), B (1488 m) and A (1987 m) are bathed by the WMDW. Bottom water

133   temperature is stable through the part of the water column studied here (~13.1°C)

134   (Xavier Durrieu de Madron, pers. com.). Salinity ranges between 38.4 and 38.5. The

135   multicorer allowed sampling of the first decimeters of the sediment, the overlying

136   bottom waters, and an undisturbed sediment-water interface. Cores were sliced for

137   foraminiferal studies with a 0.5-cm resolution down to 4 cm, followed by 1 cm slices

138   down to 10 cm depth. Sediments were put in an ethanol-Rose Bengal mixture (95%

139   ethanol with 1g/l Rose Bengal), in order to identify living (stained) specimens. For

140   more detailed information about methods, please consult Fontanier et al., (2008).

141

142

143   **2.2 Pore water geochemistry**

144   Sediment sampling for pore water extraction was carried out under an inert

145   atmosphere (N_2). Hereafter, samples were centrifuged at 3500 rpm for 20 min. The

146   supernatant was filtered and acidified (HNO_3 *s.p.*) for analyzing dissolved metals.

147   Dissolved Mn concentrations were determined with flame atomic absorption

148   spectrometry (Perkin Elmer AA 300). Precision for this method is ± 5%. A pore water

149   subsample was also analyzed for Mn using ICP-MS (Agilent 7500 Series). Relative

150   precision for this method is 3%. Total alkalinity of pore water was measured at

151   Utrecht University using an automated titrator (702 SM Titrino, Metrohm) making

152   Gran plots. Dissolved Inorganic Carbon (DIC) was measured using a Dissolved

153   Carbon Analyser (Shimadzu, Model TOC-5050A). Carbonate ion concentrations were

154   calculated using the CO2SYS software (version 01.05; Lewis and Wallace, 1998).

155   Analytical uncertainty for the alkalinity is about 10 μeq, relative standard deviation

156   for the DIC analyses is 0.8%.

157   Oxygen concentration profiles were determined using Clark-type

158   microelectrodes (Unisense©, Denmark). Labile organic matter was derived from the

159   sum of lipids, amino acids and sugars measured in the top cm of sediment; for details,

160   see Fontanier et al., 2008.

161

162   **2.3 Foraminiferal trace metal geochemistry**

163   Foraminiferal trace element concentrations were determined using two laser ablation

164   ICP-MS systems. Prior to laser ablation, all samples were gently cleaned in methanol

165   (x1) and UHQ water (x4). Between each rinse, the samples were placed in a sonic

166   bath for several seconds to thoroughly clean the tests. Benthic foraminifera from 745

167   m (station D), 980 m (station C), 1488 m (station B) and 1987 m (station A) were

168   measured at Utrecht University using a deep UV (193nm) ArF excimer laser (Lambda

169   Physik) with GeoLas 200Q optics. Ablation was performed at a pulse repetition rate

170   of 10 Hz, and energy density of 1.4 J/cm^2, with a crater size of 80μm. Ablated

171   particles were measured by a quadrupole ICP-MS (Micromass Platform) equipped

172   with a collision and reaction cell. Such a collision and reaction cell improves

173   carbonate analyses by eliminating interferences on mass 44. Scanned masses included

174   ^{24}Mg, ^{26}Mg, ^{27}Al, ^{42}Ca, ^{43}Ca, ^{55}Mn, ^{88}Sr, ^{137}Ba, ^{138}Ba, ^{208}Pb. Benthic foraminifera

175   from stations F (350 m) and E (552 m) were analyzed at ETH-Zurich (due to

176   laboratory renovations at Utrecht University). The laser type and ablation parameters

177   were identical to those detailed above. The ablated particles were measured using a

178   quadrupole ICP-MS (ELAN 6100 DRC, Perkin-Elmer). In both cases, calibration was

179   performed using an international standard (NIST610) with Ca as an internal standard

180 (Jochum et al. 2011). The same masses as measured in Utrecht were monitored, in

181 addition to ^{7}Li, ^{23}Na, ^{47}Ti, ^{60}Ni, ^{61}Ni and ^{89}Y. Inter-laboratory compatibility was

182 monitored using a matrix-matched calcite standard.

183   Analytical error (equivalent to 1 sigma), based on repeated measurement of an

184 external standard, was <5% for reported elements. Each laser ablation measurement

185 was screened for contamination by monitoring Al and Pb. On encountering surface

186 contamination, the data integration interval was adjusted to exclude any Al or Pb

187 enrichment. Cross-plots between Al and Pb versus Mn showed that they are unrelated,

188 confirming accuracy of the integrations.

189   During the laser ablation analyses the different trace elements were monitored

190 with respect to time, thus representing a cross section of the test wall. This allows not

191 only quantification of the different trace metals of interest, but also to observe

192 variability within individual tests. Each species has a distinct test-wall thickness,

193 permitting the study of intra-test variability. A typical ablation profile for *H. elegans*

194 is shown in Fig. 2.

195

196 **2.4 Analyses of manganese in foraminiferal tests**

197 Contamination and presence of secondary Mn-rich coatings on benthic foraminiferal

198 tests has been a longstanding challenge in trace metal analyses of benthic foraminifera

199 (Boyle 1983, Lea and Boyle 1989). In this study the trace metal data are based

200 exclusively on living (Rose Bengal stained) foraminifera, which effectively rules out

201 the impact of Mn-rich coatings on trace metal concentrations. At the time of sampling,

202 the collected tests were still enveloped by foraminiferal cytoplasm, preventing the

203 formation of extraneous inorganic precipitates. Although benthic foraminifera live

204 within the sediment, their test is physically separated from the environment as they

205   are enveloped in an organic sheath (Ní Fhlaithearta et al., 2013). In case a recently

206   deceased foraminifer was mistakenly analyzed (still with sufficient protoplasm to

207   stain with Rose Bengal) the Mn oxide would not only have had limited time to

208   develop, but it would also show up as a Mn spike at the start of a laser ablation profile.

209   The ablation profiles confirm that no Mn-rich phases are present at the test surfaces

210   (Fig. 2).

211   Comparing LA-ICP-MS data with traditional solution analyses for

212   foraminiferal Mg/Ca values showed that data are directly comparable (Rosenthal et al.,

213   2011). Also for trace metals such as Ni^{2+}, Cu^{2+} and Mn^{2+}, cross-calibration of LA-

214   ICP-MS and micro-XRF shows those analytical results are robust (Munsel et al.,

215   2010).

216

217   **2.5 Benthic foraminiferal Mn/Ca**

218   Manganese incorporation in benthic foraminiferal test carbonate was analyzed from 4

219   different species (*Hoeglundina elegans, Melonis barleeanus, Uvigerina mediterranea,*

220   *Uvigerina peregrina*), from 6 coring sites, for up to 9 depths in the sediment. Sample

221   coverage for all stations is described in Table 2. Descriptive statistics are presented in

222   Table 3.

223

224   **2.5.1 Intra-individual variability**

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.

227   From the other species two analyses were performed per test. The resolution of the

228   ablation profiles themselves does not allow quantifying changes in trace metals within

229   the test wall. Still, comparing the data within individual ablation profiles shows that

230   the intratest variability is generally limited for Mn (Table 4). As the ablation profiles

231   target one chamber mostly, this does not include the full potential range. Comparing

232   different ablation profiles between chambers in a single shell would circumvent this,

233   but this data is somewhat limited.

234

235   **2.5.2 Distribution characteristics of Mn/Ca in benthic foraminiferal calcite**

236   Boxplots are used to describe the range of Mn/Ca values and how the distribution,

237   median, average and skewness compares between species.. All ICP-MS

238   measurements are included, and as such represent both intra- and inter-individual

239   variation.

240

241   **3. Results**

242   **3.1 Pore water data**

243   Pore water dissolved manganese (Mn^{2+}) concentrations were measured at all six

244   stations. Manganese concentrations increase below the oxygen penetration depth at

245   stations C and D (Fig. 3), with the highest in-sediment Mn^{2+} concentrations reached at

246   station D. At stations E and F manganese concentrations remain low after crossing the

247   oxygen penetration depth. At stations A and B the oxygen penetration depth and

248   MnO_2/Mn^{2+} redox boundary are deeper than 10 cm's. Dissolved inorganic carbon

249   (DIC) and total alkalinity (TA), were measured at stations E, C and B (Fig. 4). At

250   stations D, C and E, DIC concentrations in the top 10 cm have a similar range (2350-

251   2700 µmol/kg). The DIC profile at station B has a narrower range, ranging from

252   2400-2550 µmol/kg. Total alkalinity values range from 3242 µmol/kg at station E to a

253   minimum of 2774 at station B. Carbonate ion concentrations [CO_3^{2-}] were derived

254   based on TA and DIC values. The [CO_3^{2-}] profiles were relatively similar (Fig. 4) for

255 stations E and C and B. Values for all three stations ranged from a maximum of 419

256 µmol/kg at station E to a minimum of 192 µmol/kg at station C (Fig. 4).

257 3.2 Mn/Ca data

258 3.2.1 Intra-individual variability

259 For most species some Mn/Ca analyses were below detection limit, except for *M.*

260 *barleeanus,* which contained measurable quantities of Mn in all shells analyzed. This

261 was most evident for *H. elegans*, where all but three Mn/Ca measurements were

262 below detection limit (dl). *Uvigerina peregrina* had a wider range of Mn/Ca values

263 than *U. mediterranea*. *Melonis barleeanus* exhibited the largest range of Mn/Ca

264 values of the four studied species (Fig. 5). For all species, except *H. elegans,* values

265 are somewhat skewed towards higher values.

266

267   3.2.3 Foraminiferal Mn/Ca variation across a depth transect

268 A trend of decreasing manganese incorporation with increasing water depth (350-

269 1987 m) is most clearly visible in *M. barleeanus* (Fig. 6), except that the maximum

270 values are observed at station E at 552 m. *Melonis barleeanus* shows the highest

271 Mn/Ca values and the largest Mn/Ca variability. Station E registers the broadest

272 Mn/Ca variability, which decreases with increasing water depth. *U. peregrina* also

273 exhibits the largest variability in Mn/Ca values at station E. For *U. peregrina*, Mn^{2+}

274 incorporation decreases from 350 m to 1987 m, except for station D (745 m), where

275 Mn/Ca values (between the 10 – 90th percentile) are approximately equivalent to those

276 at station A (350 m; Fig. 6). For *U. mediterranea* a trend of decreasing Mn

277 incorporation with increasing depth is found in specimens of *U. mediterranea* from

278 the sediments at 552, 745 and 980 m. The highest values are reached at the shallowest

279 station (350 m). Station E is also marked by the highest minimum Mn/Ca values for *U.*

280 *mediterranea*. At station A only two *U. mediterranea* measurements are above the

281 detection limit. *Hoeglundina elegans* shells from three stations (350 m, 1488 m and

282 1987 m) were analyzed, however, all but three measurements were below detection

283 limit (Fig. 6). These slightly elevated values were recorded at the shallowest station

284 (station F). These Mn/Ca values are still very low compared to ranges in Mn/Ca

285 values observed for the other species (Fig. 6).

286 Variability in Mn/Ca increases together with the overall Mn/Ca concentration

287 within benthic foraminiferal species (Table 4). This suggests that even at those

288 stations and depth levels where the highest Mn concentrations are recorded,

289 individuals with relatively low amounts of Mn in their calcitic test were found.

290 Comparing relative standard deviations, as a measure for the inter-specimen

291 variability, for the different stations and species suggests that with increasing Mn

292 concentration for *M. barleeanus* and *U. mediterranea* variability increases, whereas

293 for *U. peregrina* it decreases.

294

3.2.4 In-sediment variation

296 For most species Mn/Ca values are more or less constant with in-sediment depth (Fig.

297 3). However, *M. barleeanus* shows increasing Mn/Ca values with in-sediment depth.

298 This is most apparent at the shallowest station (station F - 350 m) (Fig. 3d).

299

4. Discussion

301

302 Incorporation of Mn in benthic foraminiferal carbonate depends both on foraminiferal

303 ecology and early diagenesis in sediments. Although other factors such as temperature,

304 sea water carbonate chemistry, growth rate etc., might also affect the uptake of Mn in

305 the shell carbonate (Koho et al., 2017), these effects are most likely several orders of

306 magnitude smaller compared to the large range in dissolved Mn in pore water. Since

307 pore water Mn is the dominant factor controlling Mn incorporation, studies must

308 account for ecological controls, like foraminiferal depth habitat preference, as well as

309 for geochemical controls like oxygen concentrations and organic matter fluxes (Koho

310 et al., 2015; De Lange, 1986; Reichart et al., 2003).

311

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

314 In general, flux of organic matter arriving at the sea floor decreases with increasing

315 water depth, due to ongoing degradation during settling (Arndt et al., 2013 and

316 references theirein). Consequently, redox boundaries within the sediment generally

317 also deepen as a function of water depth, as oxygen consumption in the sediment

318 decreases. Such a fundamental organic matter-depth relation is in line with the much

319 deeper oxygen penetration depths at stations A and B compared to the more shallow

320 stations. At station F the relative shallow oxygen penetration depth observed is in line

321 with its' relative shallow water depth, although the organic matter which arrives here

322 at the seafloor apparently undergoes winnowing (Fontanier et al., 2008). The organic

323 matter along the transect studied is concentrated at a so-called depocenter, which

324 largely coincides with the depths of stations C and D (Fontanier et al., 2008). As

325 bottom waters at all stations are well oxygenated, organic matter concentration can be

326 considered the main control for redox conditions at stations F-A, with the amount of

327 organic matter arriving at the seabed being regulated by water depth and sedimentary

328 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

332   explanation for this observation is that a lower porosity at F (56% versus 76% and

333   79 % at stations D and E, respectively) impedes oxygen diffusion through the

334   sediment. Alternatively, the pore water profile reflects an earlier organic matter

335   deposition event, with this organic matter being largely consumed at the time of

336   sampling. The pore water profiles require more time to re-equilibrate to the new

337   conditions (Burdige and Gieskes, 1983). At station E there is a mismatch between

338   oxygen penetration depth and the Mn^{2+} redox boundary as the Mn^{2+} redox boundary is

339   considerably deeper than the OPD. Although this is in line with the observed higher

340   bioirrigation at this station (Fontanier et al., 2008), this might reflect non-equilibrium

341   conditions as well.

342   The vertical distribution of benthic foraminiferal species varies between

343   stations, in accordance with organic matter concentrations and redox zonation, which

344   is consistent with the TROX model (Jorissen et al., 1995; Fontanier et al., 2008). In

345   case of a shallower redox zone, infaunal benthic foraminifera biomineralize in contact

346   with Mn-enriched pore water, with highest dissolved manganese concentrations

347   occurring just below the oxygen penetration depth at all stations, except for station E

348   (552 m). This is in contrast to low bottom-water oxygen environments often studied in

349   the context of proxy development studies, where pore water Mn^{2+} is released from the

350   pore water (Koho et al., 2015, 2017; Mangini et al., 2001).

351   The species studied here cover the range of shallow-infauna to intermediate-

352   infauna niches. *Hoeglundina elegans*, a typically shallow infaunal species, is often

353   found close to the sediment-water interface (Jorissen et al., 1998; Schönfeld 2001;

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354 Fontanier et al., 2002; Fontanier et al., 2008) and contains the lowest concentration of

355 Mn in its test. Only at the shallowest station (350 m) three specimens of *H. elegans*

356 show concentrations above the detection level, with values still low compared to the

357 values observed for the other species (Fig. 6). In the Bay of Biscay Reichart et al.

358 (2003) also suggested that elevated Mn concentrations in *H. elegans* were confined to

359 stations with oxygen depleted bottom waters and/or with a shallow oxygen

360 penetration depth. *Uvigerina mediterranea* and *Uvigerina peregrina* are also classed

361 as shallow-infaunal species; they are typically found within the top few centimeters of

362 the sediment column (Fontanier et al. 2002, Fontanier et al. 2008). The calculated

363 average living depth (ALD_{10}) as calculated in Fontanier et al. (2008) is consistently

364 shallower than the ALD_{10} for *U. mediterranea*. This is at odd with previous reports

365 suggesting *U. peregrina* has a slightly deeper microhabitat than *U. mediterranea*

366 (Fontanier et al. 2002; 2006). That *U. peregrina* has a deeper microhabitat is further

367 supported by the usual distinct $\partial^{13}C$ offset in *U. peregrine,* which is more depleted

368 compared to *U. mediterranea* (Schmiedl et al., 2004; Fontanier et al, 2002, 2006). The

369 higher Mn/Ca values observed here for *U. peregrina* (Figure 6) supports the idea that

370 it calcifies somewhat deeper in the sediment compared to *U. mediterranea*.

371 Alternatively, *U. peregrina* may migrate downwards within burrows to track food

372 resources, recording redox steepness (Loubere et al., 1995). This could highlight a

373 disparity between the assumed living depth (the depth interval of recovery) and

374 biomineralization depth of foraminifera. Still, this would also result in a higher

375 variability of Mn/Ca values at higher Mn/Ca levels, which is not observed. Hence,

376 more likely the observed disparity between the geochemical signals incorporated into

377 foraminiferal calcite and depth of recovery in *U. peregrina* reflects opportunistic

378 behaviour, with calcification at a shallower in-sediment depth in response to more

379 favourable conditions after e.g. seasonal peaks in organic matter fluxes (Accornero et

380 al., 2003), when the OPD is close to the sediment water interface.

381 *Melonis barleeanus*, generally considered an intermediate-infaunal species

382 (Fontanier et al., 2002, 2008), contains the highest concentrations of Mn in its test.

383 Manganese incorporation in this species increases with increasing labile organic

384 matter (Fig. 7a).

385 In summary, the habitat preference of the benthic foraminiferal species studied

386 here is reflected in the Mn/Ca values recorded in their tests. This is in contrast with

387 other results showing lower Mn/Ca values in foraminiferal tests with shallower redox

388 fronts (Koho et al., 2015). This, however, critically depends on the Mn being released

389 to the water column, which only occurs when the bottom waters are disoxic. In case

390 of a seasonal organic matter deposition event, an increase of Mn concentration in

391 foraminiferal test carbonate would initially occur in the deeper and ultimately also in

392 the more shallow calcifying foraminifera. This is in line with the conceptual

393 TROXCHEM[3] model, with the conditions studied here falling within the first stage of

394 the temporal succession considered in the model. Bottom water remains well

395 oxygenated (O_2 concentrations at the study area: 199-219 μmol/l (Fontanier et al.,

396 2008)) and organic matter loading is controlling Mn^{2+} concentrations in the sediment.

397 To what extend species are high in Mn/Ca depends on living depth and opportunistic

398 behavior.

399 At a given location, a benthic foraminiferal species' depth preference or

400 biomineralization depth, is reflected in its average Mn/Ca value (Fig. 5). The trend

401 across a depth transect shows a strong correlation to labile organic matter

402 concentrations in the surface sediments (Fig. 7). The strong correlation between labile

403 organic matter (i.e. sedimentary lipid content) and Mn incorporation in shallow and

404   intermediate infaunal species *U. mediterranea* ($R^2 = 0.80$ ($p < 0.05$) suggests that test

405   Mn has potential as a proxy for detecting past labile organic matter fluxes. Notably,

406   *M. barleeanus* has a very strong correlation (0.81), though this correlation lacks

407   statistical significance ($p > 0.05$). In contrast, *U. peregrina* shows a correlation

408   coefficient of only 0.45 (R^2) between test Mn and labile organic matter. *Uvigerina*

409   *peregrina* is reported to respond opportunistically to the concentration and quality of

410   organic matter produced during bloom events (Fontanier et al., 2003; Koho et al.,

411   2008; Barras et al., 2010). This response is in the form of increased reproduction and

412   growth. Perhaps *U. peregrina* calcifies at shallow depths and therefore does not

413   capture the Mn^{2+} gradient.

414   At low oxygen concentrations Mn is released through the reduction of

415   manganese (oxy)hydroxides. Here we show an increase in Mn/Ca incorporation in

416   several species, from shallow to intermediate-depth infaunal habitats, as a function of

417   oxygen penetration depth. Such a correlation agrees with studies by Ní Fhlaithearta et

418   al. (2010) and McKay et al. (2015) from a down core record of Mn/Ca$_{H. elegans}$ during

419   the formation of sapropel (S1) in the Eastern Mediterranean and a paleoproductivity

420   study of an upwelling system in the NE Atlantic, respectively. Here, a comparison of

421   Mn (oxy)hydroxides in the sediment and foraminiferal Mn^{2+} showed that Mn^{2+}

422   incorporation in an epifaunal to shallow infaunal species was higher during times of

423   enhanced Mn^{2+} remobilization and hence higher pore water Mn^{2+}. Such a correlation,

424   however, requires that the bottom waters remain somewhat oxygenated to retain the

425   dissolved Mn^{2+} in the pore water. With disoxic bottom waters Mn^{2+} escapes the

426   porewater and foraminiferal Mn/Ca values decrease (Koho et al., 2015). However,

427   with high organic matter deposition, which might be concentrated in events, also

428   foraminiferal species living at or close to the sediment water interface may show

429   elevated Mn concentrations.

430   In addition to the here observed changes, biomineralization could affect Mn^{2+}

431   incorporation. To date, however, no studies have been carried out under controlled

432   conditions to constrain species-specific offsets in Mn incorporation. In a controlled

433   laboratory study by Munsel et al (2010) Mn incorporation in *Ammonia tepida*

434   increased with increasing Mn^{2+} concentrations in the culture water and the partition

435   coefficient was well above 1. The lack of any appreciable discrimination argues

436   against a major biomineralization impact on Mn^{2+} partitioning. Also our data does not

437   suggest a major impact of biomineralization on Mn incorporation.

438   In summary, Mn incorporation seems primarily controlled by pore water

439   conditions in close proximity to the test, with a secondary control determined by the

440   ability of a foraminifer to seasonally calcify and migrate within the sediment.

441

442   **4.2 Pore water Mn dynamics and foraminiferal migration within the sediment**

443   Manganese is incorporated in foraminiferal carbonate with a partition coefficient (D)

444   close to 1 (Munsel et al., 2010), which argues for a minor biomineralization control.

445   We calculated Mn partition coefficients for *U. mediterranea*, *U. peregrina* and *M.*

446   *barleeanus* at stations E, C and B (Table 6) based on average Mn/Ca_{foram} and average

447    $Mn/Ca_{pore\ water}$ values found above the Mn^{2+}-MnO(H) redox boundary. Calculated D_{Mn}

448   agrees with the previously reported D_{Mn} by Munsel et al., (2010), with values varying

449   between ~1-2 for *U. mediterranea* and *U. peregrina*. The Mn partition coefficient for

450   *Melonis barleeanus* ranges from ~4-7. The partition coefficient for this species most

451   likely reflects its capacity to calcify under dysoxic conditions, close to or even below

452   the oxygen penetration depth. Still, this calculation is based on two assumptions: (1)

453   the depth foraminifera are recovered from during sampling corresponds with the

454 average depth of calcification and, (2) variation in pore water is limited. Establishing

455 species specific Mn partitioning coefficients using culture experiments might,

456 however, be needed for unlocking the full potential of this proxy.

457 A foraminifer calcifying within a steep Mn^{2+} gradient is exposed to a higher

458 range of Mn^{2+} concentrations (over a fixed depth interval) compared to specimens

459 living along a more gradual Mn^{2+} concentration gradient. Since foraminifera can

460 migrate through the sediment as a response to food availability and oxygen

461 concentrations (Alve and Bernhard 1995; Gross, 2000), not only the slope of the Mn

462 gradient, but also the in-sediment depth range (microhabitat) of the foraminifer in

463 relation to the Mn redox boundary, should be considered (Fig. 8). A shallow-infauna

464 species, with a limited in-sediment range, would be expected to exhibit lower

465 variability than an intermediate- infauna species, which possibly migrates

466 considerably in depth. This is exemplified at station F (350 m) where we note an

467 increase in foraminiferal test Mn/Ca variability at 2 cm depth, consistent with the

468 oxygen penetration depth at that station (Fig. 3). Moreover, the variability in Mn/Ca

469 values increases towards higher Mn/Ca values. This is in line with *M. barleeanus*

470 traveling more actively through the redox zones than *U. mediterranea* or *U. peregrina*.

471 Nitrate respiration could be mechanism allowing this dynamic behaviour by *M.*

472 *barleeanus* in the intermediate depth habitat. However, Pina-Ochao et al. (2010),

473 studying denitrification in foraminifera, reports nitrate storage in all three species

474 mentioned here. Notably, nitrate storage in *M. barleeanus* is lower than *U.*

475 *mediterranea* and *U. peregrina*. Alternatively *M. barleeanus* thrives in habitats with

476 varying oxygenation and hence also varying Mn levels, whereas the stable but high

477 Mn/Ca values in the Uvigerinids are related to their opportunistic behaviour.

478   With a redox-sensitive element such as Mn, in a dynamic geochemical

479   environment, it is not surprising that foraminifera exhibit high inter-individual

480   variability in their Mn/Ca incorporation. Benthic foraminifera reside in a 3D

481   geochemical mosaic, as reflected by a large spread of Mn values, in addition to

482   undergoing substantial temporal variability. Still, using Mn/Ca as a potential proxy

483   for redox conditions or primary productivity seems promising, as established

484   ecological characteristics of species are reflected by differences in Mn incorporation.

485   Apparently the large variability on both spatial and temporal scales averages out,

486   making Mn into a promising proxy for paleo-redox and organic matter flux.

487

488   **5. Conclusion**

489   This study investigates the link between benthic foraminiferal habitat preferences and

490   manganese incorporation in their tests. Manganese incorporation increases with

491   bottom-arriving labile organic matter content, driven by enhanced oxygen demand.

492   This results in a more shallow oxygen penetration depth with immediately below it

493   enhanced dissolved Mn levels. Shallow infaunal species calcify under lower

494   concentrations of Mn compared to intermediate infauna, in line with their depth

495   preference. Their depth habitat is related to in-sediment changes in redox conditions.

496   However, these distribution not necessarily vary synchronous with changes in redox

497   zonation as illustrated by the Mn/Ca variability in their tests (Fig. 8). The latter

498   reflects the Mn/Ca porewater composition, which itself is directly related to reactive

499   organic matter concentration and redox conditions. The foraminiferal Mn/Ca ratio and

500   inter-specimen variability, therefore, provides information on past Mn cycling within

501   the sediment. Consequently, the foraminiferal Mn/Ca ratio is a potential proxy for

502   bottom-water oxygenation and organic matter fluxes.

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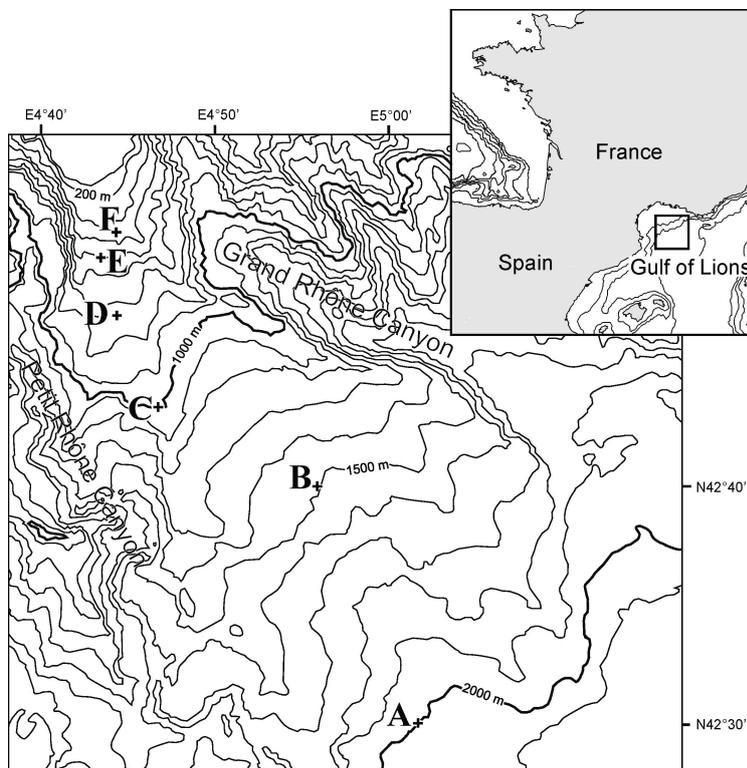
Figure 1. Location map showing sampling stations and bathymetry.
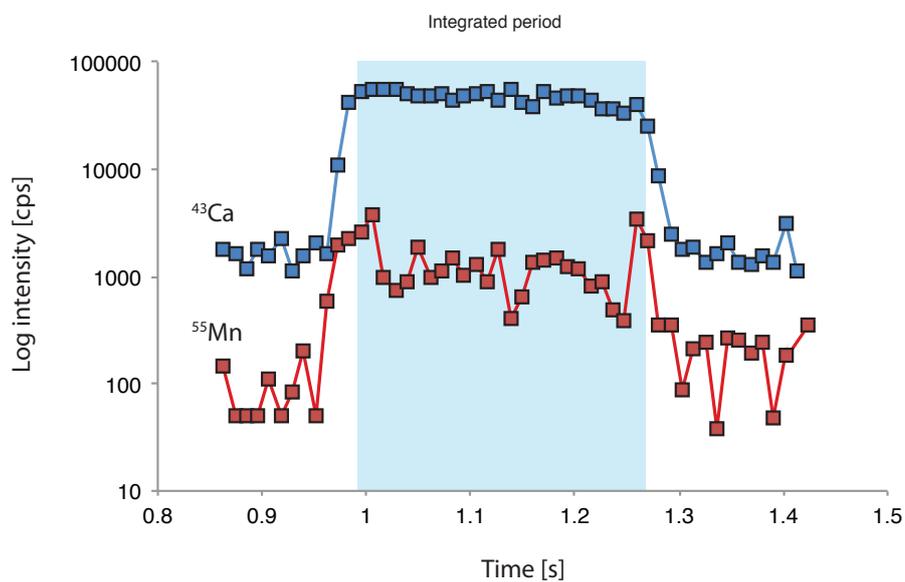
Figure 2. Example of a laser ablation profile, signal log intensity counts per second [cps] through time. The integrated signal is shaded.
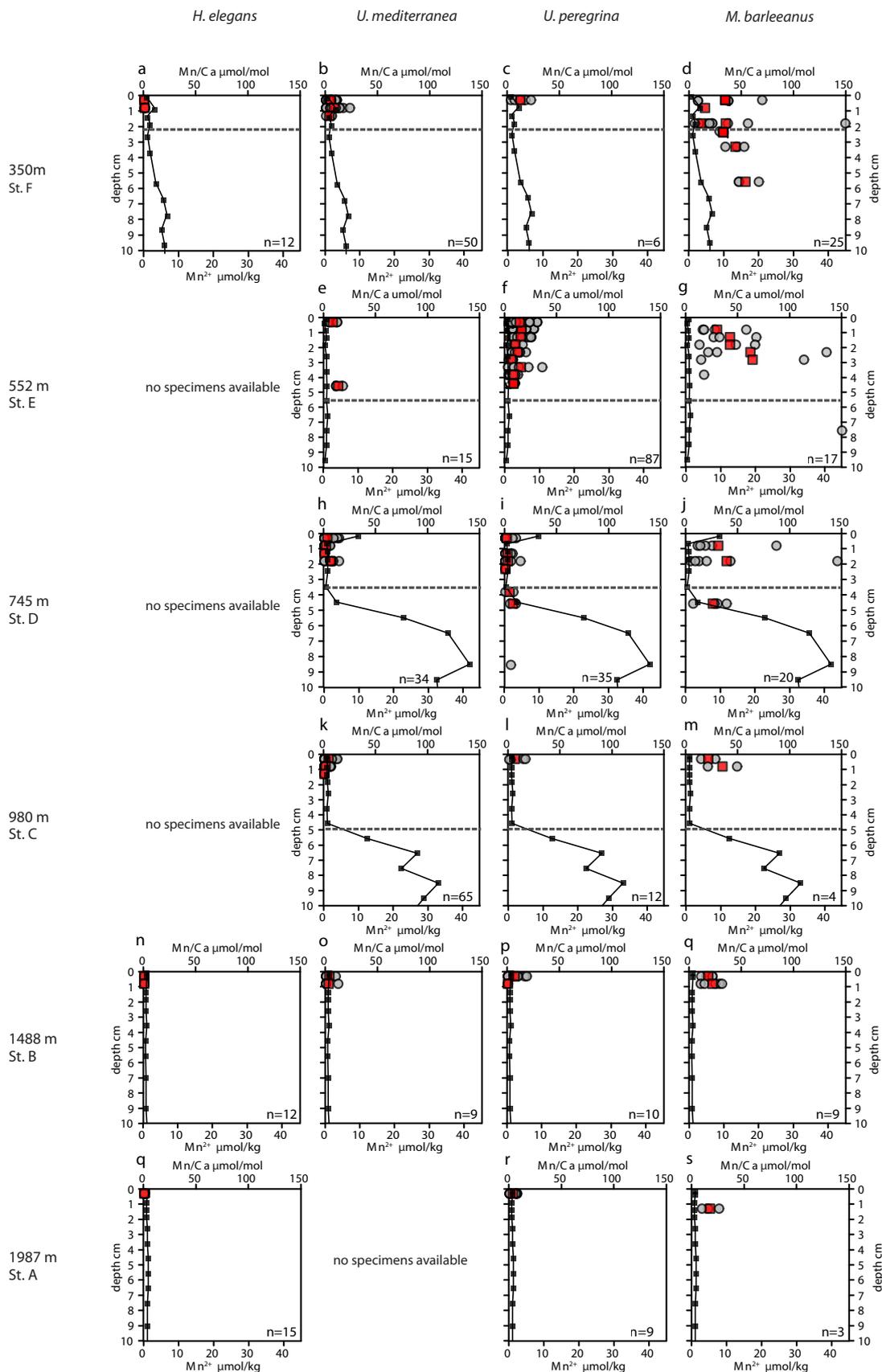
Figure 3. Plots of Mn/Ca (µmol/mol) measured in living (stained) Hoeglundina elegans, Uvigerina mediterranea, Uvigerina peregrina and Melonis barleeanus. Individual analyses are plotted (grey circles) alongside average values for a given depth in the sediment (red squares). Porewater Mn2+ (µmol/kg) profiles (black line) are plotted for all stations. The dashed grey line indicates the oxygen penetration depth (OPD).

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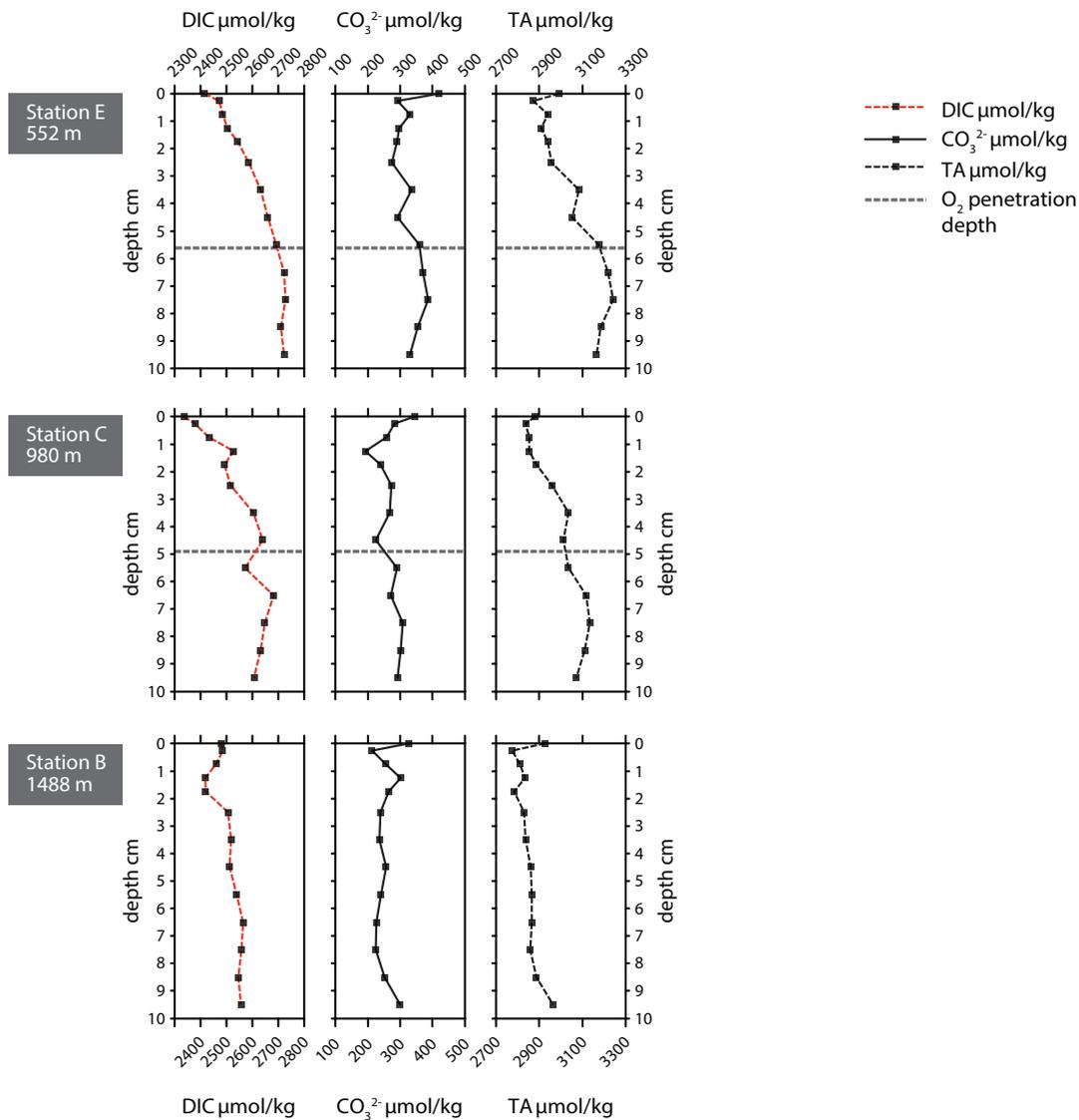
Figure 4.

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.
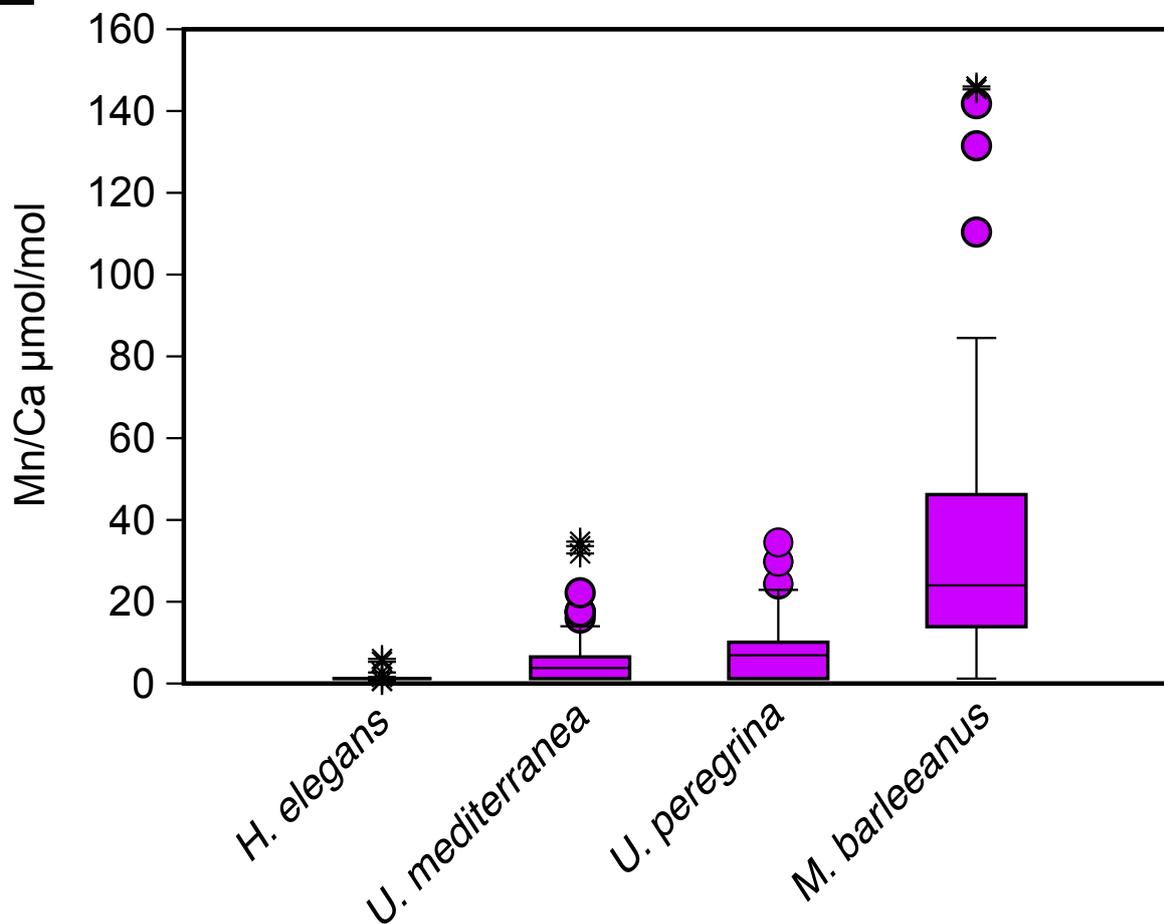
Figure 5. Box plots describing the distribution in Mn/Ca values measured in living (stained) individuals of Hoeglundina elegans, Uvigerina mediterranea, Uvigerina peregrina and Melonis barleeanus. The box represents all values between the 25th and 75th percentile. The dissection line through the box 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.
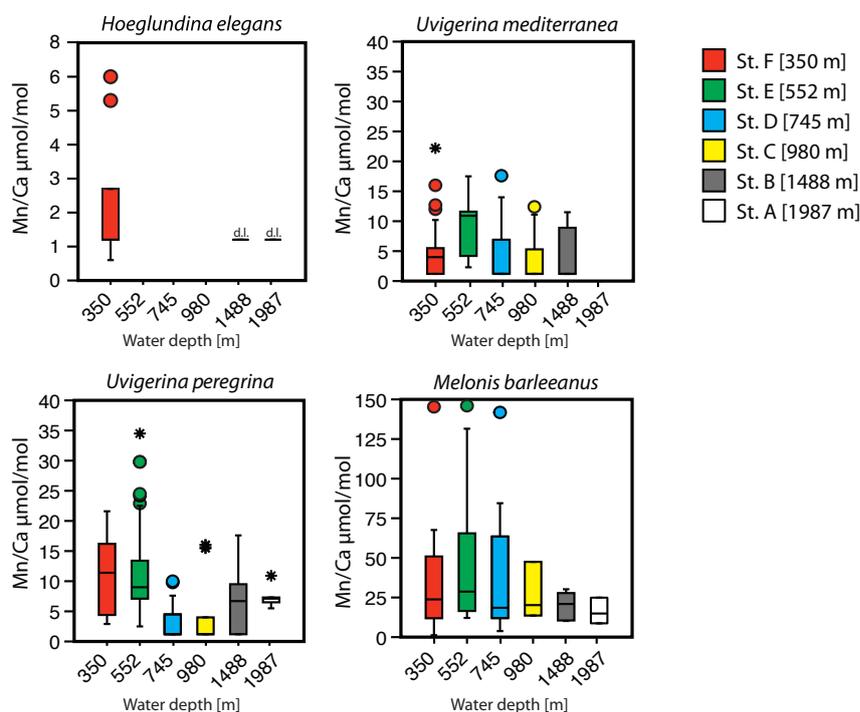
Figure 6. Box plots describing the distribution of Mn/Ca values across a depth transect (350-1987 m) measured in living (stained) individuals of Hoeglundina elegans, Uvigerina mediterranea, Uvigerina peregrina and Melonis barleeanus. Note that the scale of the y-axis varies. The box represents all values 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.
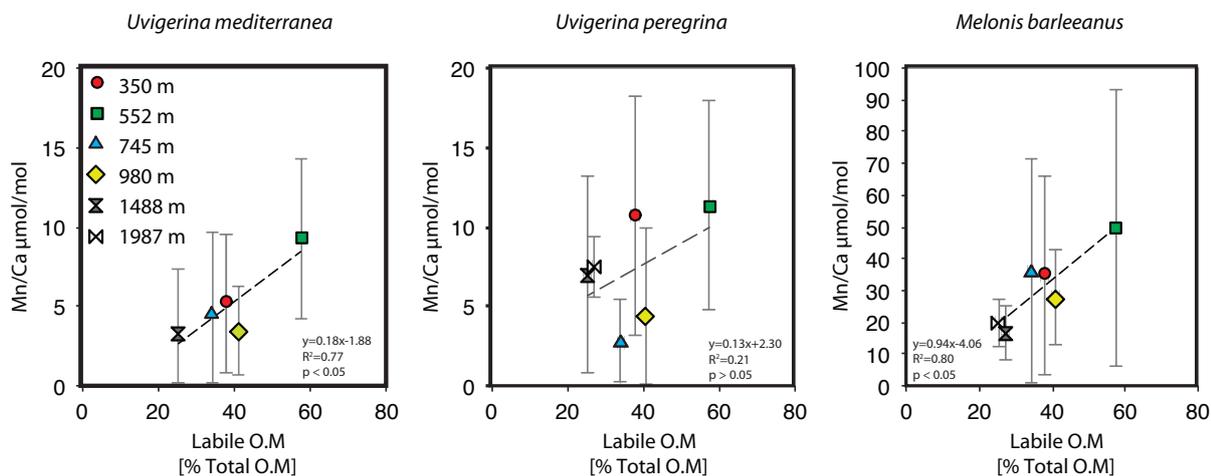
Figure 7. Plots of average Mn/Ca µmol/mol versus labile organic matter [% Total Organic matter].
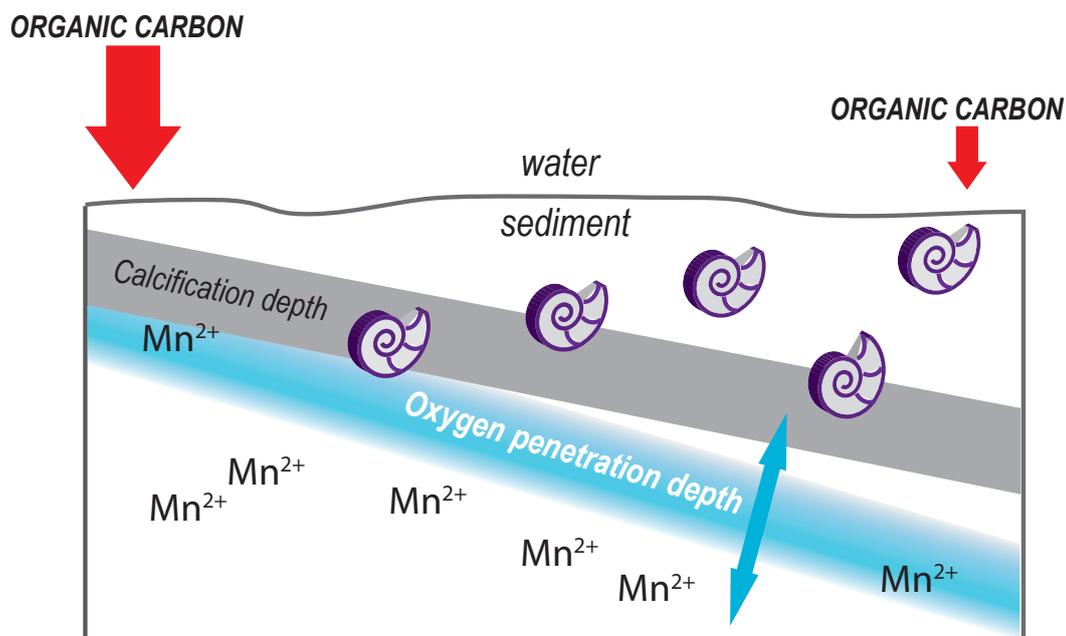
Figure 8. Schematic diagram of a shallow-infaunal and intermediate-infaunal benthic foraminifera and their spatial relationship with the sediment redox boundaries, migration zone, ALD and calcification depth.

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. barleeanus*, for all specimens recovered above the reported oxygen penetration depth (Fontanier et al., 2008).