

1 **Determination of the Mg/Mn ratio in foraminiferal coatings: an approach**
2 **to correct Mg/Ca temperatures for Mn-rich contaminant phases**

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12

13 **Abstract**

14 **The occurrence of manganese-rich coatings on foraminifera can have a significant effect**
15 **on their bulk Mg/Ca ratios thereby biasing seawater temperature reconstructions. The**
16 **removal of this Mn phase requires a reductive cleaning step, but this has been suggested**
17 **to preferentially dissolve Mg-rich biogenic carbonate, potentially introducing an**
18 **analytical bias in paleotemperature estimates. In this study, the geochemical**
19 **composition of foraminifera tests from Mn-rich sediments from the Antarctic Southern**
20 **Ocean (ODP Site 1094) was investigated using solution-based and laser ablation ICP-MS**
21 **in order to determine the amount of Mg incorporated into the coatings. The analysis of**
22 **planktonic and benthic foraminifera revealed a nearly constant Mg/Mn ratio in the Mn**
23 **coating of ~0.2 mol/mol. Consequently, the coating Mg/Mn ratio can be used to correct**
24 **for the Mg incorporated into the Mn phase by using the down core Mn/Ca values of**

25 **samples that have not been reductively cleaned. The consistency of the coating Mg/Mn**
26 **ratio obtained in this study, as well as that found in samples from the Panama Basin,**
27 **suggests that spatial variation of Mg/Mn in foraminiferal Mn overgrowths may be**
28 **smaller than expected from Mn nodules and Mn-Ca carbonates. However, a site-specific**
29 **assessment of the Mg/Mn ratio in foraminiferal coatings is recommended to improve the**
30 **accuracy of the correction.**

31 **1. Introduction**

32 Foraminiferal Mg/Ca ratios show strong temperature sensitivity owing to the temperature-
33 dependent partitioning of Mg during calcification, with more Mg incorporated into the
34 carbonate when ambient seawater temperatures are higher (e.g. Nürnberg et al., 1996;
35 Rosenthal et al., 1997; Lea et al., 1999). During the past two decades, foraminiferal Mg/Ca
36 thermometry has been successfully used to reconstruct past temperature changes in the
37 surface and deep ocean (e.g. Lea et al., 2000; Barker et al., 2009; Elderfield et al., 2012).
38 Reliable seawater temperature reconstructions require the removal of extraneous material that
39 may bias the Mg/Ca ratio away from that of the biogenic carbonate. Cleaning procedures
40 designed for Mg/Ca paleothermometry routinely involve the removal of clays and organic
41 matter (Elderfield and Ganssen, 2000; Barker et al., 2003; Rosenthal et al., 2004). The
42 removal of Mn-rich contaminant phases requires an additional reductive step (Boyle and
43 Keigwin, 1985), but there has been some debate as to whether their removal is necessary. On
44 the one hand, if Mn-rich phases associated with foraminifera have Mg/Mn ratios typical for
45 marine Mn nodules and Mn-Ca carbonates, on the order of 0–0.4 mol/mol (e.g. Cronan, 1975;
46 Peacor et al., 1987; Baturin, 1988; de Lange et al., 1992; Wen et al., 1997), measured Mn/Ca
47 ratios of 0.1 mmol/mol would imply a bias in the original Mg/Ca ratio by only about 0.02
48 mmol/mol. This is insignificant in most cases and supports the argument for omitting a
49 reductive step (Barker et al., 2003). On the other hand, the potential presence of Mn-rich
50 phases with high Mn/Ca ratios (Boyle, 1983; Pena et al., 2005; 2008) would argue in favor of

51 the inclusion of a reductive cleaning step (Martin and Lea, 2002; Pena et al., 2005, 2008; Bian
52 and Martin, 2010).

53 However, the reductive cleaning step has been shown to adversely affect the Mg/Ca ratio of
54 the remaining, cleaned, biogenic carbonate, lowering the Mg/Ca ratio of core-top and low-Mn
55 samples much more than expected from Mg/Mn estimates for the Mn-rich contaminant phase
56 (Barker et al., 2003; Rosenthal et al., 2004; Elderfield et al., 2006; Yu et al., 2007; Yu and
57 Elderfield, 2008; Bian and Martin, 2010). Although there is some debate about the exact
58 mechanism involved (Yu et al., 2007; Bian and Martin, 2010), this offset in Mg/Ca has been
59 attributed to the selective removal of Mg from the carbonate lattice. Incongruent dissolution
60 of carbonates has also been observed during acid leaching experiments and post-depositional
61 dissolution on the sea floor, indicating that Mg-rich carbonate is more dissolution-prone than
62 low-Mg carbonate (Russel et al., 1994; Brown and Elderfield, 1996; Rosenthal et al., 2000;
63 Haley and Klinkhammer, 2002; Benway et al., 2003; Barker et al., 2003; Sadekov et al.,
64 2010; Fehrenbacher and Martin, 2014). Due to the bias introduced by reductive cleaning, it
65 has been recommended to omit this step and to clean foraminifera according to the method
66 published by Barker et al. (2003) (Barker et al., 2003; Yu et al., 2007; Yu and Elderfield,
67 2008). While this may be a valid approach for most samples considered for
68 paleoceanographic research, there is a need for alternative strategies for samples that are
69 significantly contaminated by Mn-enriched phases.

70 In this study, we demonstrate that a promising solution to this potential problem is to
71 quantitatively determine the Mg/Mn ratio in the Mn-rich phase of the foraminifera used for
72 Mg/Ca thermometry. The combination of solution-based and laser ablation inductively
73 coupled plasma mass spectrometry (solution-based ICP-MS and LA-ICP-MS, respectively)
74 applied to chemically cleaned Mn-enriched planktonic and benthic foraminifera allows
75 differentiation between the Mg/Mn ratio of the material removed during reductive cleaning
76 and the Mg/Mn ratio of the Mn-rich contaminant. If the coating Mg/Mn is constant over time,

77 the obtained ratio can be employed to correct for Mg in the contaminant phase using the
78 foraminiferal Mn/Ca down core record following the equation

$$\frac{Mg}{Ca_{corrected}} = \frac{Mg}{Ca_{ox}} - \left(\frac{Mn}{Ca_{ox}} \times \frac{Mg}{Mn_{coating}} \right) \quad (1)$$

79 where the subscript *ox* represents the *oxidative* cleaning procedure.

80 **2. Study area**

81 The samples selected for this study are from Ocean Drilling Project (ODP) Site 1094 (53.2°S,
82 05.1°E, water depth of 2807 m) retrieved from the Atlantic sector of the Southern Ocean
83 south of the Antarctic Polar Front. The study site is currently bathed by Circumpolar Deep
84 Water and is well ventilated, sitting immediately downstream of newly formed Antarctic
85 Bottom Water (AABW) (Jaccard et al., 2016). Recent studies have suggested that the deep
86 South Atlantic underwent large changes in oxygenation both on millennial and glacial-
87 interglacial timescales (e.g. Jaccard et al., 2016; Gottschalk et al., 2016). These changes in
88 oxygenation stem from a combination of decreased deep water production and increased
89 organic matter remineralization (and thus oxygen demand) resulting from increased iron
90 fertilization during past ice ages (Jaccard et al., 2016). The sediments are thus characterized
91 by significant changes in redox conditions thereby affecting the sedimentary incorporation of
92 redox-sensitive trace metals, such as Mn and U (Hayes et al., 2014; Jaccard et al., 2016).
93 Jaccard et al. (2016) recently reported substantial sedimentary Mn accumulations during the
94 last glacial termination, illustrating the return to oxic conditions at times when remineralized
95 carbon was released back to the atmosphere. A literature compilation showed that these Mn
96 peaks had previously been reported from South Atlantic sediments and more broadly from the
97 equatorial- and subarctic Pacific (e.g. Jaccard and Galbraith, 2012; Jaccard et al., 2016). As
98 such, the conditions encountered at the study site may be more common than previously
99 assumed.

100 **3. Background and experimental approach**

101 A 1.5 Ma long planktonic *N. pachyderma* (s.) Mg/Ca record (n = 988) has been established at
102 ODP Site 1094 (Figure 1). The foraminifera were picked from a relatively narrow size
103 fraction (mostly 200–250 μm ; on rare occasions 150–250 μm), and cleaned following the
104 protocol outlined by Barker et al. (2003), i.e. omitting the reductive step (see details in
105 Section 4.2). The results reveal a positive correlation between Mg and Mn, over a range of
106 Mn/Ca ratios up to 3.2 mmol/mol (Figure 1a), with shell weight changes having only a small
107 impact on their covariation. Mn/Ca in unaltered planktonic foraminiferal carbonate collected
108 from plankton tows, sediment traps and sediment core-tops (e.g. Boyle, 1983; Russell et al.,
109 1994; Eggins et al., 2003; Barker et al., 2003) are typically well below 0.05 mmol/mol,
110 suggesting that most of the Mn is of post-depositional origin. Application of Mg/Ca
111 paleothermometry (using the calibration by Vázquez Riveiros et al., 2016) to interglacial
112 sequences with high Mn accumulation at this site resulted in unrealistically high sea surface
113 temperatures (SST) of more than 10 °C. This temperature overestimation in sediments with
114 high Mn enrichment, as well as the clear positive correlation of Mg and Mn points to the
115 incorporation of Mg into the Mn-rich contaminant phase.

116 A closer examination of the correlation between Mg and Mn in Figure 1a shows that only a
117 small portion of the variance can be explained by a linear fit ($r^2 = 0.03$) for samples with
118 Mn/Ca lower than 0.1 mmol/mol. Consequently, Mg/Ca values that are accompanied by low
119 Mn/Ca primarily reflect Mg variations in the calcite lattice that vary with ambient seawater
120 temperature. In contrast, the correlation coefficient for Mn-rich foraminifera samples (Mn/Ca
121 > 0.5 mmol/mol) is relatively high ($r^2 = 0.57$), with Mg/Ca varying primarily due to changes
122 in post-depositional Mn accumulation. Around one third of these Mn-rich samples are from
123 two short-lived spikes within Marine Isotope Stage (MIS) 9 and 11, where Mn/Ca correlates
124 strongly with Mg/Ca ($r^2 = 0.96$ and 0.89 , respectively) (Figure 1b).

125 The main goal of this study is the analytical determination of the Mg/Mn ratio in the coatings
126 of foraminifera from ODP Site 1094 in order to be able to correct for the Mg present in the
127 Mn-rich phases. The Mg/Mn ratio of the Mn-rich phase can be determined by taking the

128 difference in Mg/Ca and Mn/Ca between samples cleaned using the oxidative and the
129 reductive cleaning protocol, respectively, and can be obtained by

$$\frac{\Delta x}{\Delta Mn} = \frac{\left(\frac{x}{Ca}\right)_{red} - \left(\frac{x}{Ca}\right)_{ox}}{\left(\frac{Mn}{Ca}\right)_{red} - \left(\frac{Mn}{Ca}\right)_{ox}} \quad (2)$$

130 where x represents the element of interest, and subscripts *red* and *ox* represent the *reductive*
131 and *oxidative* cleaning procedures, respectively.

132 The *N. pachyderma* (s.) samples were selected to cover several depth intervals characterized
133 by high Mn levels ($n = 75$, 125–950 ka), representing foraminiferal Mn/Ca ratios ranging
134 from 0.1 to 3.2 mmol/mol (Figure 1a). The experiment conducted on *N. pachyderma* (s.) was
135 complemented by investigation of the planktonic species *Globigerina bulloides* ($n = 10$,
136 332–401 ka) and *Globorotalia puncticuloides* ($n = 7$, 332–335 ka), and the benthic species
137 *Melonis pompilioides* ($n = 25$, 335–1450 ka) and *Melonis barleanum* ($n = 2$, 1164–1408 ka)
138 whenever their respective abundances were high enough to allow meaningful analysis. All
139 these samples were analyzed by solution-based ICP-MS to obtain bulk trace element ratios. In
140 addition, five of the samples (0.8–3.2 mmol/mol Mn/Ca), along with two samples with
141 minimal coating (< 0.05 mmol/mol Mn/Ca), were analyzed by laser ablation ICP-MS to
142 investigate the spatial distribution of trace elements within and on the surfaces of the
143 foraminifera.

144 **4. Methods**

145 **4.1 Cleaning strategy**

146 The polar species *N. pachyderma* (s.) in sediments of ODP 1094 have very low shell weights
147 (3–10 μg per individual picked from the 200–250 μm size fraction) and are thus prone to
148 dissolution during chemical cleaning. A preliminary test showed that the reductive reagent
149 (Boyle and Keigwin, 1985), applied to a subset of *N. pachyderma* (s.) samples, dissolved
150 more than 80 % of the carbonate for average starting shell weight of less than ~ 7 μg . In this

151 study, an attempt was made to minimize sample loss by reducing the corrosivity of the
152 reagent applied.

153 Although reductive cleaning was originally designed to facilitate the removal of Mn and Fe
154 oxides from the test surface by reducing Mn^{4+} and Fe^{3+} to soluble Mn^{2+} and Fe^{2+} (Boyle and
155 Keigwin, 1985), this step has also been shown to be efficient in removing Mn-rich carbonate
156 phases (Pena et al., 2005). The reductive reagent commonly used consists of 31 M hydrous
157 hydrazine (N_2H_4), 16 M ammonium hydroxide (NH_4OH), and a solution of 0.25 M citric acid
158 ($C_3H_5O(COOH)_3$) and 16 M ammonia (NH_3), mixed together in proportions of 1/8:1:1
159 (Boyle and Keigwin, 1985; Yu et al., 2007). In this study, the concentrations of hydrazine and
160 ammonium citrate (with molarities of 1.75 M and 0.13 M in the standard solution,
161 respectively) were reduced to 50 % and 25 % of their original concentrations in order to
162 decrease citrate-induced carbonate dissolution (Yu et al., 2007; Bian and Martin, 2010). In
163 samples with abundant *N. pachyderma* (s.) and high shell weight (38 of 75 samples), the
164 reductive cleaning step was applied to three subsets of foraminifera samples using three
165 different reductive cleaning solutions: the standard reductive solution, and the two more dilute
166 solutions. Additionally, the “25 %” reductive reagent solution was applied to replicate
167 samples in 28 cases, in order to test the reproducibility of the results. As shown below, the
168 results revealed that the “25 %” reductive cleaning solution was able to remove the majority
169 of the Mn-rich coating, leading to the decision to apply this less corrosive reductive reagent
170 solution to the samples where foraminifera were sparse and/or shell weights were low.
171 Because the planktonic foraminifera *G. bulloides* and *G. puncticuloides* are generally larger
172 and more robust than the *N. pachyderma* (s.) in the samples considered here, they were
173 cleaned using both the standard and “25 %” reductive solution along with some replicates for
174 the latter method where sufficient material was available. The benthic foraminifera were
175 cleaned using the standard reductive cleaning solution only, as a preliminary test revealed that
176 the diluted solutions were not able to remove the Mn phases adequately.

177 **4.2 Cleaning procedures**

178 Depending on their shell weight and the abundance of the foraminifera, a varying number of
179 well-preserved and visibly clean individuals (usually > 300 µg and > 40 planktonic and > 9
180 benthic individuals) were picked for each of the cleaning procedures applied. The planktonic
181 foraminifera were selected from a relatively narrow size range (*N. pachyderma* (s.): 200–250
182 µm; *G. bulloides* and *G. puncticuloides*: 355–425 µm), and the benthic foraminifera were
183 picked from the >150 µm size range. Prior to cleaning, foraminifera tests were weighed and
184 gently crushed between two glass plates under a microscope to allow contaminant phases to
185 be removed during cleaning (Boyle and Keigwin, 1985). The crushed material was then
186 transferred to acid cleaned thin walled 500 µl polypropylene vials (Greaves, 2008). The
187 oxidative cleaning procedure applied in this study is that published by Barker et al. (2003).
188 Briefly, clays were removed by multiple rinses with ultra-purified water and methanol.
189 Organic matter was removed by oxidation in a hot alkali-buffered (0.1M NaOH) solution of 1
190 % hydrogen peroxide (H₂O₂). Subsequently, the test fragments were checked under a
191 microscope to remove any remaining silicates. Finally, samples were leached with 0.001M
192 double distilled HNO₃ to remove any adsorbed contaminants from the foraminifera tests. The
193 reductive cleaning protocol includes all steps described above, but with an additional step to
194 remove trace metal enriched Fe-Mn contaminant phases (Boyle, 1981; Boyle and Keigwin,
195 1985). Briefly, after the clay removal step, 100 µl of reductive cleaning solution was added to
196 each sample, which was then placed into a hot water bath for 30 minutes.

197 **4.3 ICP-MS analysis**

198 The cleaned foraminifera material was dissolved in ~300 µl 0.1M double distilled HNO₃,
199 centrifuged for 5 minutes (5000 rpm) and transferred to trace-metal cleaned Savillex PFA
200 vials, leaving 30 µl of solution behind to avoid contamination from any non-carbonate solid
201 impurity. Element/Ca ratios were measured by ICP-MS at ETH Zurich using a single
202 collector, high-resolution magnetic-sector Thermo Scientific Element XR instrument. The
203 instrument was tuned for maximum sensitivity, concurrently paying attention to oxide and

204 hydride production and isobaric and molecular interferences. Samples were introduced into
205 the plasma via a self-aspirating microconcentric nebulizer (flow rate of 100 $\mu\text{l}/\text{min}$) in
206 conjunction with a quartz cyclonic spray chamber. Element/Ca ratios were calculated using a
207 synthetic in-house standard. Results were corrected for instrument and dissolution-acid blank
208 (on average three orders of magnitude smaller than a typical sample). Accuracy and precision
209 of the instrument were assessed by routine measurements of six gravimetrically prepared
210 consistency standards of which two are in-house standards (Mg/Ca and Mn/Ca) and four are
211 standards from the University of Cambridge (Mg/Ca) (Greaves et al., 2005). The standards
212 have a composition similar to foraminiferal carbonate and were run at similar Ca
213 concentrations (Greaves et al., 2005). The consistency standards measured throughout the
214 past 20 months are within $0.9\% \pm 3.6\%$ (2 SD) and $0.6\% \pm 4.2\%$ (2 SD) of the gravimetric
215 value for Mg/Ca and Mn/Ca, respectively. The average long-term reproducibility of Mg/Ca
216 and Mn/Ca is $\pm 2.6\%$ (2 RSD) and $\pm 2.2\%$ (2 RSD), respectively.

217 **4.4 LA-ICP-MS analysis**

218 Laser ablation ICP-MS was performed on oxidatively cleaned foraminifera (excl. leaching;
219 Vetter et al., 2013) from 7 samples selected to cover the entire range of Mn concentration
220 ($0.02\text{--}3.2$ mmol/mol Mn/Ca; Figure 1). The laser ablation system consists of a GeoLas
221 (Coherent) 193 nm ArF excimer laser coupled to an Elan 6100 DRC (Perkin Elmer)
222 quadrupole ICP-MS. The sample was targeted by a laser fluence of ~ 2 J/cm^2 that ablated a
223 layer 30 μm in diameter and about 0.1 μm in depth from the surface of the foraminifera test
224 with each laser pulse, with a repetition rate of 2 Hz. ^{24}Mg , ^{25}Mg , ^{42}Ca , ^{44}Ca , ^{55}Mn , ^{57}Fe , and
225 ^{238}U were measured by sequential peak-hopping with dwell times of $10\text{--}30$ ms. The material
226 ablated was carried via He (1.1 L/min gas flow) to the ICP-MS that had been optimized for
227 high sensitivity and a low oxide ratio (ThO/Th of $\sim 0.5\%$). Four whole foraminifera from
228 every sample were targeted at three different chambers, resulting in 12 depth profiles per
229 sample. Additionally, chamber fragments from 3 of the 7 samples were ablated towards both,

230 the outer and the inner surface. The end of the shell wall was identified as the depth where the
231 ⁴⁴Ca signal reaches an inflection point (see Figure 4a) (Vetter et al., 2013).

232 **4.5 Scanning electron microscopy**

233 Scanning electron microscopy (SEM) images were obtained using a Zeiss Supra 50 VP, with
234 a secondary electron detector, a working distance of 12 mm, and an accelerating voltage of 15
235 kV. The cleaned foraminifera fragments were mounted on carbon tape and coated with 10 nm
236 of platinum prior to analysis.

237 **5. Results**

238 **5.1 Cleaning efficiency of the reductive cleanings**

239 Mn/Ca and Mg/Ca ratios for *N. pachyderma* (s.), processed without the reductive step, and
240 cleaned using the standard, the “50 %”, and the “25 %” reductive cleaning solution, are
241 shown in Figure 2a–b. Reductive cleaning reduces Mn/Ca concentrations by 87 to 90 %, with
242 gradually increasing efficiency at higher concentrations. For samples with initial Mn/Ca
243 lower than 1 mmol/mol, reductive cleaning reduces Mn/Ca to values generally below 0.1
244 mmol/mol, independent of the concentration of the reductive solution used (average Mn/Ca
245 after reductive cleaning was 0.05, 0.06 and 0.07 mmol/mol for the standard, “50 %”, and “25
246 %” reductive cleaning solutions, respectively). In contrast, for samples with initial Mn/Ca
247 ratios ranging between 1 and 3.2 mmol/mol, the standard reductive cleaning solution is
248 slightly more efficient than the more dilute solutions, decreasing Mn/Ca values to an average
249 of 0.13 mmol/mol compared to 0.17 and 0.21 mmol/mol for the “50 %” and “25 %” reductive
250 method, respectively. Insufficient removal of Mn by reductive cleaning may be related to Mn
251 phases that are located in pores and spine holes within the test, whose reductive elimination
252 has been observed to be more difficult (Boyle, 1983; Pena et al., 2005; Pena et al., 2008)

253 SEM images obtained from oxidatively cleaned *N. pachyderma* (s.) and *G. bulloides* from
254 samples containing high bulk foraminifera Mn concentrations (3.2 and 1.9 mmol/mol Mn/Ca,

255 respectively) reveal a thin layer at the inner surface of the shell not observed in corresponding
256 tests that have undergone the reductive cleaning step (Figure 2c–d).

257 **5.2 Composition of the material removed during reductive cleaning**

258 The decrease in Mn/Ca in *N. pachyderma* (s.) following the reductive step is accompanied by
259 a significant decrease in Mg/Ca (Figure 2b). Taking the ratio of the differences in Mg/Ca and
260 Mn/Ca between oxidative and reductive cleaning (equation (2)) allows determination of the
261 Mg/Mn ratio of the material removed during reductive cleaning ($\Delta\text{Mg}/\Delta\text{Mn}$). Figure 3a shows
262 the $\Delta\text{Mg}/\Delta\text{Mn}$ ratio for the three reductive cleaning solutions applied as a function of the
263 Mn/Ca difference between the oxidatively and reductively cleaned samples ($\Delta\text{Mn}/\text{Ca}$). The
264 $\Delta\text{Mg}/\Delta\text{Mn}$ ratio decreases with increasing removal of Mn coating, approaching a constant
265 value for $\Delta\text{Mn}/\text{Ca}$ larger than ~ 1.25 mmol/mol. The reproducibility of the $\Delta\text{Mg}/\Delta\text{Mn}$ ratio for
266 the replicated samples, cleaned using the “25 %” reductive method, is relatively high for low
267 $\Delta\text{Mn}/\text{Ca}$, decreasing to 0.04 for $\Delta\text{Mn}/\text{Ca}$ greater than 1.25 mmol/mol. The three different
268 reductive cleaning solutions gave very similar results for samples with high $\Delta\text{Mn}/\text{Ca}$ (Figure
269 3b). The $\Delta\text{Mg}/\Delta\text{Mn}$ average of *N. pachyderma* (s.) with $\Delta\text{Mn}/\text{Ca} > 1.25$ mmol/mol was 0.25
270 ± 0.04 ($n = 20$, 1SD), similar to $\Delta\text{Mg}/\Delta\text{Mn}$ for *G. bulloides* (0.23 ± 0.06 , $n = 9$), and *G.*
271 *puncticuloides* (0.20 ± 0.04 , $n = 3$). The $\Delta\text{Mg}/\Delta\text{Mn}$ values of *M. pompilioides* and *M.*
272 *barleeaanum* were less dependent on the amount of the Mn phase removed, averaging $0.19 \pm$
273 0.04 mol/mol for samples with $\Delta\text{Mn}/\text{Ca} > 0.25$ mmol/mol ($n = 26$). The Fe/Mn ratio of the
274 material removed during cleaning ($\Delta\text{Fe}/\Delta\text{Mn}$) averages 0.02 ± 0.01 ($n = 70$) and 0.04 ± 0.01
275 ($n = 24$) for planktonic and benthic foraminifera with $\Delta\text{Mn}/\text{Ca} > 0.25$ mmol/mol (Figure 3d).

276 **5.3 Trace element distribution within the foraminifera test**

277 Laser ablation ICP-MS element depth profiles obtained from a series of cleaned *N.*
278 *pachyderma* (s.) from seven samples provide additional insight into the trace element
279 distribution through the shell wall and its surface. Figure 4 shows a representative selection of
280 depth profiles for three of the five investigated samples, with bulk foraminifera Mn/Ca

281 ranging from 0.8 to 3.2 mmol/mol (Figures 4a–i). The most striking feature in most of the
282 profiles is the systematic increase in Mn/Ca at the inner part of the shell wall, accompanied by
283 a smaller increase in Mg/Ca. In contrast, Fe/Ca is consistently low throughout the entire
284 profile, showing no concurrent trend with Mn/Ca or Mg/Ca (Fe is at or slightly above the
285 detection limit of ~30 ppm; Figure 4c). At the outer part of the shell Mn/Ca is typically an
286 order of magnitude lower than at the inner shell wall, but exceeds the natural range of
287 variability of (uncoated) foraminiferal carbonate from the same site by an order of magnitude
288 (Figure 4j). The accumulation of the Mn phase within the biogenic carbonate makes it
289 practically impossible to define a clear boundary between carbonate and secondary Mn
290 coating, particularly if the Mn enrichment is small (e.g. Figure 4g, 4h). In order to investigate
291 the relationship between Mn and Mg within the higher coated intervals systematically, the
292 Mn-rich part of the depth profile is specified as coating from the point where the Mn/Ca value
293 is twice as large as the test Mn/Ca close to the outer surface (i.e. the average Mn/Ca of the
294 outermost ~1 μm of the profile). Although the definition of the boundary is somewhat
295 arbitrary, it allows us to investigate the Mg/Mn of the Mn phase more quantitatively. From
296 the 86 laser ablation profiles that have been produced on samples with high bulk Mn/Ca
297 values, 49 profiles, measured on 30 different foraminifera, registered an identifiable increase
298 in Mn/Ca.

299 The Mn/Ca profiles within the coated intervals show a gradual increase towards the inner
300 surface where the maximum Mn/Ca ratio is reached (Figures 4a–i). The pattern of Mn/Ca
301 enrichment (gradual to sharp), its lengthscale (~0.2–4 μm), and the values at the inner surface
302 (~1–14 mmol/mol) all show significant variation, even within a single foraminifer. Mg/Mn
303 within the foraminifera tests decreases with increasing Mn concentration, showing ratios of
304 ~0.3–1.4 at the inner surface of the shell (Figures 4a–4i). This large range of Mg/Mn is
305 explained by the variability of Mn/Ca in coatings and its dominant effect on the Mg/Mn ratio.
306 Importantly, coating Mn/Ca and Mg/Mn correlate negatively (Figure 4k–4l). While low
307 Mn/Ca values correspond to Mg/Mn ratios that are very variable, Mg/Mn ratios level off with

308 higher Mn/Ca. The profiles that resulted from ablation from the inner to the outer surface
309 record higher Mn/Ca values at the inner surface, with their Mg/Mn (~0.2 to 0.4) approaching
310 the value determined by bulk measurements of planktonic and benthic foraminifera.

311 **6. Discussion**

312 **6.1 Origin of Mn-rich foraminifera coatings**

313 Mn phases associated with foraminifera tests are Mn-oxyhydroxides and Mn-rich carbonates
314 (Boyle, 1981, 1983; Pena et al., 2005, 2008). As the saturation of seawater with respect to Ca-
315 Mn carbonate requires very high dissolved Mn concentrations (Pedersen and Price, 1982;
316 Landing and Lewis, 1991), sedimentary Mn-rich phases are thought to be originally
317 precipitated as Mn-oxyhydroxides, which then potentially dissolve upon burial and when
318 oxygen-depleted conditions are encountered (Calvert and Pedersen, 1993, 1996). Reduction
319 of Mn⁴⁺ to soluble Mn²⁺ is a prerequisite for the dissolution of Mn oxyhydroxides, a process
320 that will increase the concentration of dissolved Mn in porewaters (Calvert and Pedersen,
321 1993; King et al., 2000). Mn is then removed from porewater by the formation of Mn-rich
322 carbonates, preferentially forming at the inner surface of foraminifera tests due to the even
323 more reductive microenvironment (Murray, 1991) and the reactive surfaces that promote
324 nucleation (Pedersen and Price, 1982; Mucci, 2004).

325 The laser ablation depth profiles through coated tests of *N. pachyderma* (s.) show consistently
326 elevated Mn/Ca values at the inner surface of the shell, corroborating the SEM images that
327 revealed a coating of unknown nature at the inner surface of *N. pachyderma* (s.) and *G.*
328 *bulloides*. Systematic enrichments in Mn/Ca at the innermost margin of foraminifera shells
329 have also been observed in *Neogloboquadrina dutertrei* from the Panama basin (Pena et al.
330 2005, 2008). Pena et al. 2005 have identified the Mn phase as a kutnohorite, a Ca-Mn
331 carbonate with typically 5–10 mol% MgCO₃ (Peacor et al., 1987). In contrast to Mn-
332 oxyhydroxides, which are often accompanied by Fe-rich phases, Fe is generally low in Ca-Mn
333 carbonates (Peacor et al., 1987; Calvert and Pedersen, 1996). The present study did not

334 involve mineralogical analysis of the contaminant phase due to the large amount of
335 foraminiferal material required. However, the suboxic conditions prevailing within the
336 sediments of ODP 1094 (Shipboard Scientific Party, 1999; King et al., 2000) suggest that the
337 Mn-rich contaminant phase is likely a carbonate, as preservation of oxyhydroxides is only
338 possible where the environment remains oxic (Calvert and Pedersen, 1996). This is
339 corroborated by the low Fe/Mn ratios of the material removed during cleaning (Figure 3d)
340 and the lack of correlation between Fe and Mn within the coatings, as shown by the laser
341 ablation profiles (Figure 4c). However, we cannot completely exclude the possibility that a
342 small fraction of the Mn phase is associated with oxyhydroxides.

343 **6.2 Mg/Mn in foraminifera coatings**

344 The Mg/Mn ratio of the material removed during reductive cleaning varies with the amount of
345 Mn-rich contaminant eliminated, leveling off with increasing $\Delta\text{Mn}/\text{Ca}$ (Figure 3a–c). To our
346 knowledge, the only other study that has investigated the effect of reductive cleaning on
347 foraminifera from Mn-rich sediments is that of Pena et al. (2005). Their measurements,
348 conducted on the planktonic foraminifera *N. dutertrei* and *Globigerinoides ruber* from the
349 Panama Basin, show a similar trend, with lower $\Delta\text{Mg}/\Delta\text{Mn}$ values associated with removal of
350 greater amounts of coating material (Figure 3c). Similarly, the $\Delta\text{Mg}/\Delta\text{Mn}$ ratio remains stable
351 for samples with $\Delta\text{Mn}/\text{Ca} > \sim 1.25$ mmol/mol (0.19 ± 0.07), although the range of bulk
352 foraminifera Mn/Ca values is twice as large as in our study. There could be two possible
353 interpretations of the hyperbolic curvature: that the coating Mg/Mn varies with the degree of
354 Mn contamination, or that Mg/Mn is constant in the Mn-bearing phase and another process
355 leads to the observed variation in $\Delta\text{Mg}/\Delta\text{Mn}$.

356 If $\Delta\text{Mg}/\Delta\text{Mn}$ were controlled only by the variation of Mg/Mn in the Mn contaminant phase,
357 then our results would imply that Mg is less readily incorporated into the Mn phase if Mn
358 concentrations increase in the latter. Mg/Mn ratios in natural Ca-Mn carbonates compiled by
359 Peacor et al. (1987) tend to decrease with higher MnCO_3 contents (Figure 5). Furthermore,

360 Mucci (1988) showed in laboratory experiments that the amount of Mg incorporated in
361 carbonate overgrowths decreases with increasing MnCO₃ content of the precipitated solid,
362 further corroborating the suggestion that the Mg/Mn ratio in Ca-Mn carbonates decreases
363 with increasing MnCO₃ content (Figure 5b).

364 While acknowledging that Mg/Mn can vary with the MnCO₃ content, the following
365 arguments argue against substantial variation of MnCO₃ in coatings of foraminifera from
366 ODP Site 1094. First, the strong linear correlation of bulk *N. pachyderma* (s.) Mg/Ca and
367 Mn/Ca in two defined intervals within MIS 9 and 11 indicate that the variation in Mg/Mn in
368 samples from ODP 1094 cannot be large (Figure 1b). Second, a close variation between
369 MnCO₃ content and coating Mg/Mn would imply that $\Delta\text{Mg}/\Delta\text{Mn}$ changes uniformly for all
370 the foraminifera species, and over the entire $\Delta\text{Mn}/\text{Ca}$ range. In contrast, the variation of
371 $\Delta\text{Mg}/\Delta\text{Mn}$ in samples from this study and the Panama Basin where a lot of coating has been
372 removed is small, while the benthic species show almost no variation at all (Figure 3c).

373 Given that Mg/Mn varies only within a narrow range in the Mn phase accumulating on the
374 inner foraminifera surface, the $\Delta\text{Mg}/\Delta\text{Mn}$ ratio of the samples would be expected to cluster
375 around a nearly constant value. If this assumption is true, then we require another explanation
376 for the variations in $\Delta\text{Mg}/\Delta\text{Mn}$ observed in this study, and in samples from the Panama Basin.
377 Previous studies have demonstrated that Mg is preferentially removed from carbonate during
378 reductive cleaning (e.g. Barker et al., 2003; Rosenthal et al., 2004; Yu et al., 2007; Bian and
379 Martin, 2010), which would result in greater deviation from the Mg/Mn endmember of the
380 Mn coating the smaller the contribution of the contaminant. The coating end member
381 dominates $\Delta\text{Mg}/\Delta\text{Mn}$ with increasing amount of material removed, which constrains the
382 coating Mg/Mn value for all the planktonic foraminifera investigated to 0.24 ± 0.05 , and for
383 the benthic foraminifera to 0.19 ± 0.04 . The good correspondence of the Mg/Mn ratio
384 between the different foraminifera species, which are from sediments whose age ranges from
385 125 to 1450 ka, indicates that the amount of Mg incorporated into the Mn-rich coatings is
386 species-independent and temporally stable. The slightly lower average of the two benthic

387 species is consistent with the observation that benthic foraminifera are usually less affected by
388 preferential dissolution during reductive cleaning (Yu et al., 2007; Yu and Elderfield, 2008),
389 implying that their coating Mg/Mn average of 0.19 ± 0.04 is more reliable. This value is close
390 to the average Mg/Mn ratios observed in Mn nodules (Table 1) and Ca-Mn carbonates (Figure
391 5c).

392 Laser ablation depth profiles through shells of *N. pachyderma* (s.) reveal great variation in
393 Mn/Ca and Mg/Mn at the inner surface of the shell, within a single profile as well as between
394 profiles from the same foraminifer and sample. However, coating Mn/Ca and Mg/Mn are
395 correlated, with decreasing Mg/Mn ratios for high Mn/Ca values. Given that Mg/Mn in
396 inorganic Mn-rich carbonates coated on foraminifera is consistent across foraminifera species,
397 the variations in Mn/Ca and Mg/Mn might be due to increasing accumulation of the Mn phase
398 in pores close to the inner surface of the test as observed by Pena et al. (2008), leading to an
399 increased proportion of biogenic carbonate ablated with the Mn phase as the inner test surface
400 is approached. Furthermore, the rounded test surface of the small spherical *N. pachyderma*
401 (s.) hinders a perpendicular ablation of the target, increasing the probability of obtaining a
402 mixed signal of primary and secondary carbonate. Last, if ablation starts at the outer surface,
403 the laser beam is forced to pass through the ablation pit before ablating the higher coated
404 intervals, promoting the co-ablation of material from the adjacent shell walls. Notably,
405 highest Mn/Ca ratios at the inner surface are observed if the test is ablated from inner to outer
406 surface. Mg/Mn in these highly coated intervals matches the Mg/Mn range determined by
407 solution-based ICP-MS (Figure 4k-l).

408 **6.3 Preferential dissolution during reductive cleaning**

409 In order to quantify the extent to which Mg is preferentially dissolved from the biogenic
410 carbonate during reductive cleaning, we estimate $\Delta\text{Mg}/\Delta\text{Mn}$ for the *N. pachyderma* (s.) data
411 using the amount of coating removed ($\Delta\text{Mn}/\text{Ca}$), the Mg/Mn determined for the coatings of *N.*
412 *pachyderma* (s.), and estimates of the decrease in Mg/Ca of the carbonate during reductive

413 cleaning. The estimated $\Delta\text{Mg}/\Delta\text{Mn}$ is a function of the degree to which Mg is preferentially
 414 dissolved and is given by

$$\frac{\Delta\text{Mg}}{\Delta\text{Mn}} = \frac{\text{Mg}_{\text{coating}} + \text{Mg}_{\text{carbonate}}^{\text{lost from}}}{\text{Mn}_{\text{coating}}} = \frac{\Delta \frac{\text{Mn}}{\text{Ca}} a + \left(\frac{\text{Mg}}{\text{Ca}_{\text{ox}}} - \frac{\text{Mn}}{\text{Ca}_{\text{ox}}} a \right) f}{\Delta \frac{\text{Mn}}{\text{Ca}}} \quad (3)$$

415 where $\Delta\text{Mn}/\text{Ca}$ represents the difference in Mn/Ca between oxidatively and reductively
 416 cleaned samples, a denotes Mg/Mn in the coating, the term in brackets represents the estimate
 417 for the unaltered Mg/Ca in the carbonate, and f is the proportion of Mg that is preferentially
 418 lost from the biogenic carbonate during reductive cleaning (i.e., the extent by which Mg/Ca_{ox}
 419 is lowered). The value taken for the coating Mg/Mn (a) is 0.19 mol/mol, the average for Mn-
 420 rich coatings associated with the more dissolution-resistant benthic foraminifera from ODP
 421 Site 1094. Importantly, the outcome of the calculations is not sensitive to the exact value
 422 chosen for a . Mn in biogenic carbonate, typically well below 0.05 mmol/mol Mn/Ca (e.g.
 423 Boyle, 1983; Russell et al., 1994; Eggins et al., 2003; Barker et al., 2003), is neglected here
 424 due to its minor effect on the results.

425 Figure 6 shows the estimated $\Delta\text{Mg}/\Delta\text{Mn}$ as a function of 5 %, 15 % and 30 % preferential
 426 dissolution of Mg-enriched carbonate along with the analytically determined $\Delta\text{Mg}/\Delta\text{Mn}$
 427 values for each of the reductive cleaning methods (Figure 6a–c) and their averages (Figure
 428 6d). $\Delta\text{Mg}/\Delta\text{Mn}$ estimated assuming that 15 % of Mg is preferentially dissolved agrees well
 429 with the analytical data, its linear fit plotting close to the 1:1 line in each of the scatter plots.
 430 These results correspond well to previous studies showing that the Mg/Ca ratio of reductively
 431 cleaned core top planktonic foraminifera is ~10–15 % lower than those that have only seen an
 432 oxidative clean (Barker et al. 2003; Rosenthal et al., 2004, Bian and Martin, 2010). Other
 433 studies have shown that reductive cleaning decreases Mg/Ca of benthic foraminifera by ~8 %
 434 more than expected from Mg/Mn in Mn phases (Yu et al., 2007; Yu and Elderfield, 2008), in
 435 agreement with our assumption that benthic foraminifera are less susceptible to preferential
 436 dissolution of MgCO₃.

437 Remarkably, the degree to which Mg/Ca is offset from the value expected from the Mg/Mn
438 ratio in the Mn phase does not seem to depend on the corrosivity of the cleaning solution
439 used, although the solubility of carbonates increases with increasing citrate concentration (Yu
440 et al., 2007; Bian and Martin, 2010). This is consistent with cleaning experiments of Bian and
441 Martin (2010) showing that the Mg/Ca offset of foraminifera cleaned with varying citrate
442 concentrations are all very similar, though consistently lower compared to samples cleaned
443 with a solution containing no citrate. The leveling off of Mg/Ca with increasing corrosivity of
444 the cleaning solution suggests that the lowering of Mg/Ca during reductive cleaning does not
445 act like post-depositional dissolution (Brown and Elderfield, 1996; Sadekov et al., 2010).
446 Bian and Martin (2010) invoke other mechanisms to explain the lowering of Mg/Ca in low-
447 Mn samples after reductive cleaning, such as the preferential removal of Mg restricted to the
448 surface or to Mg-enriched portions of the test.

449 **6.4 Implications for paleoceanographic reconstructions of foraminiferal Mg/Ca** 450 **temperatures**

451 The results presented in this study confirm that Mn-rich contaminant phases associated with
452 foraminifera can have a significant impact on the Mg/Ca ratio of biogenic carbonate. When
453 translated into temperature using the recently published species-specific calibration for *N.*
454 *pachyderma* (s.) (Vázquez Riveiros et al., 2016), the Mg within the coating can produce a
455 temperature overestimation of up to 7.0 ± 2.2 °C, given the 1σ range of the Mg/Mn ratio in
456 the contaminant phase determined in benthic foraminifera (Figure 7d–f). Using the average
457 Mg/Mn ratio of 0.19 mol/mol, 14 % of the samples analyzed are shown to be contaminated to
458 a degree that leads to a temperature bias of more than 0.9 °C, equivalent to the calibration
459 uncertainty of *N. pachyderma* (s.) (Vázquez Riveiros et al., 2016). To circumvent this
460 problem, we corrected for Mg in the contaminant phase using the downcore Mn/Ca record of
461 the oxidatively cleaned foraminifera samples.

462 We applied a correction to the 1.5 Ma long *N. pachyderma* (s.) Mg/Ca record from ODP Site
463 1094, using the average Mg/Mn ratio obtained for benthic foraminifera from the same core. In
464 order to assess the sensitivity of the corrected Mg/Ca to the value for the selected Mg/Mn
465 ratio, Mg/Mn was varied within the 1σ range (Figure 7a–c). The difference between the
466 measured and the corrected Mg/Ca is small for Mn/Ca below 0.2 mmol/mol, equivalent to
467 0.25 ± 0.14 °C (75 % of all samples). In contrast, the corrected Mg/Ca for samples with
468 Mn/Ca higher than 0.2 mmol/mol show a larger and increasing deviation from the original
469 data, removing the positive trend between Mg and Mn. The degree of offset between
470 measured and corrected data is strongly dependent on the value of Mg/Mn employed, the
471 reasons for which are twofold. Firstly, the high Mn/Ca ratios obtained in this study exert great
472 leverage on the corrected Mg/Ca values. Secondly, the low sensitivity of Mg/Ca to
473 temperature at the lower end of the calibration curve (Vázquez Riveiros et al., 2016)
474 translates small Mg/Ca changes into relatively large temperature changes in these cold
475 Southern Ocean waters.

476 These observations illustrate the crucial importance of the accurate quantification of the
477 Mg/Mn ratio to correct Mg/Ca. While acknowledging that there might be some variability
478 associated with the incorporation of Mg into the Mn phase, we suggest that the average value
479 of the coating Mg/Mn obtained from the benthic foraminifera, which are less prone to
480 dissolution during reductive cleaning, is the best estimate for the Mg/Mn ratio of the Mn
481 phase in samples from ODP Site 1094. Correcting Mg/Ca using Mg/Mn = 0.19 mol/mol
482 eliminates the positive correlation between Mg and Mn observed in the oxidatively cleaned
483 samples with Mn/Ca > 0.5 mmol/mol (slope: 0.02; $r^2 = 0.02$) (Figure 7b).

484 7. Conclusions

485 SEM images and laser ablation ICP-MS profiles through foraminifera shells reveal Mn-rich
486 coatings at the inner surface of planktonic foraminifera from the Antarctic Southern Ocean
487 that can have a significant effect on the bulk foraminiferal Mg/Ca ratio. The removal of this

488 Mn phase requires a reductive cleaning step, but this is known to preferentially dissolve Mg-
489 rich biogenic carbonate. In this study, two different approaches were adopted to assess the
490 coating Mg/Mn in foraminifera from ODP Site 1094 in the Southern Ocean. First, solution-
491 based ICP-MS measurements of oxidatively and reductively cleaned Mn-rich foraminifera
492 allowed determination of the Mg/Mn ratio of the material removed during reductive cleaning.
493 Second, laser ablation ICP-MS provided high-resolution trace element profiles through coated
494 foraminifera shells, corroborating the Mg/Mn results obtained from bulk measurements. The
495 determination of the Mg/Mn ratio in foraminiferal coatings allows correction for Mg
496 incorporated into the Mn phase, by using the down core Mn/Ca record of oxidatively cleaned
497 samples from the same site.

498 Considering the various sources of Mn in the ocean and sediment, and the occurrence of
499 foraminiferal Mn overgrowths as both oxide and carbonate phases whose formation involves
500 very different processes, the incorporation of Mg into Mn-rich foraminiferal coatings is not
501 expected to be spatially constant. However, coating Mg/Mn ratios observed in samples from
502 the Panama Basin and the Antarctic Southern Ocean are very similar, which render it
503 probable that the range of Mg/Mn in foraminiferal Mn overgrowths is smaller than expected
504 from Mn-rich nodules and Mn-Ca carbonates (~0–0.4 mol/mol). In order to be able to make a
505 broader assessment of the variations in the Mg/Mn ratio in foraminiferal coatings, more
506 studies from other oceanic regions with high Mn accumulation rates would be required.

507 We recommend application of the protocol presented in this study when foraminiferal Mn/Ca
508 is high enough to introduce a significant bias to measured Mg/Ca ratios and the temperatures
509 calculated from them, for example, in excess of the calibration uncertainty of the species
510 investigated (e.g. 0.9 °C for *N. pachyderma* (s.); Vazquez et al., 2016). There is, however, no
511 absolute Mn/Ca ratio that can be taken as a threshold to indicate a ‘contaminated’ sample
512 because the degree of contamination depends on several factors such as the average Mg/Ca
513 ratios and the temperature sensitivity of the foraminifera species investigated.

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673 **Captions**

674 **Table 1.** Average Mg/Mn ratios in Mn nodules and Mn encrustations of the Atlantic, Indian,
675 and Pacific Oceans, and the average for the global ocean. Mg/Mn ratios of individual sites can
676 deviate markedly from the basin average.

677 **Figure 1.** (a) Covariance between Mg/Ca and Mn/Ca measured in oxidatively cleaned *N.*
678 *pachyderma* (s.) from sediments of ODP Site 1094, covering the past 1.5 Ma. The linear fits
679 show the correlation between the two parameters at the lower (< 0.1 mmol/mol; $r^2 = 0.03$) and
680 upper end (> 0.5 mmol/mol; $r^2 = 0.57$) of the Mn/Ca range. The white, blue, yellow, and gray
681 symbols show *N. pachyderma* (s.), *G. bulloides*, *G. puncticuloides* and *M. pompilioides*
682 samples that were used in this study. The red stars mark samples that have been investigated
683 by LA-ICP-MS. (b) Correlation of Mg/Ca and Mn/Ca for two short-lived Mn spikes within
684 MIS 9 (open symbols) and MIS 11 (solid symbols).

685 **Figure 2.** (a–b) Mn/Ca and Mg/Ca ratios for *N. pachyderma* (s.) after cleaning with three
686 different reductive solutions, compared to samples that have only been cleaned oxidatively.
687 Reductive cleaning results in a clear decrease in Mn/Ca (87–90 %) and Mg/Ca ratios (each of
688 the gray lines represents the results of a sample). (c–d) SEM images of an oxidatively cleaned
689 *N. pachyderma* (s.) and *G. bulloides* chamber fragment with high bulk Mn/Ca values show a
690 distinctive layer at the inner surface of the test. In contrast, SEM images of the same samples
691 after the reductive cleaning step show no evidence of such a layer, indicating that the Mn
692 coating at the inner surface of the test has been successfully removed.

693 **Figure 3.** The Mg/Mn and Fe/Mn ratio of the material removed during reductive cleaning
694 ($\Delta\text{Mg}/\Delta\text{Mn}$, $\Delta\text{Fe}/\Delta\text{Mn}$) as a function of the amount of Mn/Ca removed. (a) $\Delta\text{Mg}/\Delta\text{Mn}$ of the
695 different reductive cleaning solutions applied to samples of *N. pachyderma* (s.). (b) Average
696 $\Delta\text{Mg}/\Delta\text{Mn}$ of the reductive cleaning solutions for *N. pachyderma* (s.) compared to $\Delta\text{Mg}/\Delta\text{Mn}$
697 of the planktonic species *G. bulloides*, and *G. puncticuloides*, and the benthic species *M.*
698 *pompilioides* and *M. barleeianum*. (c) Compilation of $\Delta\text{Mg}/\Delta\text{Mn}$ data presented in this study

699 and samples from the Panama Basin (ODP 1240), on the latter for planktonic *N. dutertrei* and
700 *G. ruber* (Pena et al., 2005). (d) $\Delta\text{Fe}/\Delta\text{Mn}$ of planktonic and benthic foraminifera from this
701 study.

702 **Figure 4.** Representative selection of laser ablation ICP-MS Mg/Ca (black), Mn/Ca (red), and
703 Mg/Mn (blue) profiles from reductively cleaned *N. pachyderma* (s.) samples of four intervals
704 covering the entire range of Mn/Ca (0.02–3.2 mmol/mol) (a–j). In the first three rows, the
705 two plots on the left show profiles that were produced within a single foraminifer by ablating
706 towards the inner surface (a, b, d, e, g, h, j). Samples plotted in the third column were ablated
707 towards the outer surface (c, f, i). The ^{44}Ca profile, with an example shown in (a), was used to
708 identify the beginning and the end of the shell wall. The dashed line marks the boundary
709 between primary shell and coating, defined as the depth when Mn/Ca reaches twice the value
710 at the outer part of the shell. The example Fe/Ca data shown in (c) are at or only slightly
711 above the detection limit (~ 30 ppm). Note the different scales on the y-axes. (k) Negative
712 correlation between coating Mg/Ca concentrations and coating Mg/Mn ratios for all
713 measurement points within the coated intervals. (l) Negative correlation between average
714 coating Mg/Ca concentrations and average coating Mg/Mn ratios. The blue and yellow bars in
715 Figure (k) and (l) represent the coating Mg/Mn 1σ range determined by solution-based ICP-
716 MS for planktonic and benthic foraminifera.

717 **Figure 5.** (a) Compilation of natural Ca-Mn-Mg carbonates whose composition has been
718 projected onto a $\text{CaCO}_3\text{-MnCO}_3\text{-MgCO}_3$ ternary phase diagram (replotted from Peacor et al.,
719 1987). (b) Mg/Mn of all carbonates from the ternary phase diagram as a function of their
720 MnCO_3 content. Carbonates with 0.5–20 mole% Mg and 1–95 mole% Mn are highlighted in
721 black. Compositions of carbonates that have been precipitated during lab experiments from
722 artificial seawater using different Mn concentrations are shown in red (Mucci, 1988). The
723 legend in (b) is also valid for (a). (c) Histogram of Mg/Mn values in natural Ca-Mn-Mg
724 carbonates with 0.5–20 mole% Mg and 1–95 mole% Mn. Three of the 239 samples, with
725 $\text{Mg/Mn} > 1$, were excluded in calculating the Gaussian fit and the average Mg/Mn ratio.

726 **Figure 6.** Assessment of preferential dissolution for *N. pachyderma* (s.) during reductive
727 cleaning for the three different cleaning solutions applied (a–c), and the average of the
728 cleaning solutions (d). The Mg/Mn ratio of the material removed ($\Delta\text{Mg}/\Delta\text{Mn}$) is estimated by
729 using the determined Mg/Mn ratio of the coating and by varying the relative amount of Mg
730 that is preferentially dissolved between 5 % and 30 %. Comparison between the analytically
731 determined and estimated $\Delta\text{Mg}/\Delta\text{Mn}$ indicates that 15 % of the Mg in the carbonate is
732 dissolved during reductive cleaning, its linear fit plotting close to the 1:1 line in each of the
733 scatter plots (see insets). The percentage of Mg dissolved from the carbonate is independent
734 of the corrosivity of the solution used.

735 **Figure 7.** (a–c) Covariance between the measured Mg/Ca and Mn/Ca on the one hand
736 (black), and the corrected Mg/Ca and measured Mn/Ca on the other hand (yellow). The linear
737 fits indicate the correlation of Mg/Ca and Mn/Ca for Mn/Ca > 0.5 mmol/mol before (black)
738 and after correction (red). (d–f) Mg/Ca temperature overestimation owing to Mg incorporated
739 into the Mn phase as a function of the measured Mn/Ca. Correction is based on (a, d) the
740 lower bound, (c, e) the average, and (c, f) the upper bound of the obtained 1σ range of
741 Mg/Mn.