A high resolution and quasi-zonal transect of dissolved Ba in the Mediterranean Sea

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1 **A high resolution and quasi zonal transect of dissolved Ba in the**
2 **Mediterranean Sea**

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22 Abstract

23 The dissolved barium (D_Ba) data set for the Mediterranean Sea is here
24 expanded with data from a large-scale transect sampled in April 2011 (M84/3
25 cruise) at high resolution. A total of 833 seawater samples have been analyzed for
26 D_Ba. Over the basin the D_Ba content ranges from 38 to 85 nmol kg⁻¹ with local
27 deep D_Ba maxima reaching up to 172 nmol kg⁻¹. Deep D_Ba maxima are
28 associated with near bottom waters influenced by benthic processes and brine
29 waters. The water column is largely undersaturated with respect to barite (BaSO₄,
30 the main phase of particulate biogenic barium P_Ba), with water column barite
31 saturation state ranging between 0.2 and 0.6 over the basin. This new D_Ba
32 dataset shows that the general zonal distribution of D_Ba is impacted by the large-
33 scale Mediterranean circulation, as evidenced by the Levantine Intermediate
34 Water zonal and meridional progression as well as by the eastward flow of surface
35 Atlantic Water. However biogeochemical processes are also at play, as suggested
36 by an elevated D_Ba content of deep waters and by local lower D_Ba contents in
37 intermediate waters. These features could be attributed to active cycling between
38 the particulate and dissolved Ba phases. Since P_Ba barite has been recognized in
39 previous studies as a proxy for particulate organic carbon remineralization at
40 intermediate depths, the significance of local changes in the water column D_Ba
41 patterns may be key to better constrain the Ba and carbon dynamics in the
42 Mediterranean Sea.

1. Introduction

In the context of studies of the interactions between climate change and the oceanic biological carbon (C) pump, the barium (Ba) proxy is a key tracer to estimate the transfer of particulate matter and C from the water column to the sediments. Particulate biogenic barium (P_Ba) in suspended matter is mainly composed of barite (BaSO_4) crystals (Dehairs et al., 1980). Barite forms during particulate organic carbon (POC) degradation by marine prokaryotes at mesopelagic depths (100-1000 m; the depth range within which most of the POC transported from the mixed layer is degraded). In an ocean that is globally undersaturated with respect to barite (Monnin et al., 1999, Rushdi et al., 2000; Monnin and Cividini, 2006) POC sinking aggregates provide favourable microenvironments for barite precipitation. As a result, P_Ba barite is one of the few geochemical proxies for POC remineralization fluxes at mesopelagic depths (Dehairs et al., 1997, 2008; Cardinal et al., 2005; Jacquet et al., 2008, 2011, 2015).

It has been shown that dissolved Ba (D_Ba) behaves as a bio-intermediate element, i.e. showing low concentrations in surface waters without reaching total depletion and increasing concentrations with depth (Chan et al., 1977, Östlund et al., 1987; Jeandel et al., 1996; Jacquet et al., 2005). This distribution is mainly attributed to P_Ba cycling involving barite formation and dissolution. The Ba dynamics have been investigated in a previous study in the Southern Ocean by comparing temporal changes of dissolved and particulate barium contents and by calculating the degree of Ba conservation (Jacquet et al., 2007). It has been concluded that D_Ba displays a non-conservative behaviour at horizons of mesopelagic POC remineralization, pointing to a measureable removal of D_Ba

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68 from the local seawater by barite formation (Jacquet et al., 2007). However, much
69 remains unknown with regards to the significance of local changes in D_Ba
70 patterns to further constrain Ba dynamics and POC transfer efficiency in the water
71 column.

72 The Mediterranean Sea (MedSea) is a landlocked sea with limited, but
73 crucial, exchange with the Atlantic Ocean, two deep overturning cells, one
74 shallow circulation and a complex upper layer circulation with several permanent
75 and quasi-permanent eddies. During the Holocene period (10.8 to 6.1 cal ka BP),
76 the eastern Mediterranean suffered a major phase of climatic shift in thermohaline
77 circulation causing abrupt changes in bottom water oxygenation and deposition of
78 organic-rich anoxic sediment (sapropel). In the light of these past events, the
79 biogeochemistry and dynamics of the circulation in the Western and Eastern
80 Mediterranean (WMed, EMed), their connection and the possible implication for
81 the regional climate system are thus key issues under debate (Tanhua et al.,
82 2013b; Malanotte-Rizzoli).

83 The MedSea is also a basin of contrasting ecosystems, from strongly
84 oligotrophic deep interiors to eutrophic northern Adriatic (Durrieu de Madron et
85 al., 2011; Reygondeau et al., 2013). The coupling between surface biology and
86 internal remineralization, timescales of their variability between sub-basins and
87 discrepancies between mesopelagic trophic regime and respiration dynamics
88 (Santinelli et al., 2010, 2014; Lopez-Sandoval et al., 2011; Luna et al., 2012) are
89 for instance issues that need to be resolved for a better understanding of the bio-
90 geochemical processes involved in the carbon dynamics of the Mediterranean
91 basin. Open questions relates to the impact of the predicted changes in key
92 physical (e.g. increased stratification, salinity) on this dynamics.

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93 The present work provides a unique D_Ba dataset for the Mediterranean
94 basin. The high sampling resolution offers unprecedented opportunity to discuss
95 differences in the water column D_Ba distribution and the water column
96 saturation with respect to barite between WMed and EMed, and to investigate the
97 respective roles of physico-chemical and biogeochemical controls. This work is
98 part of a broader investigation aiming at improving the use of Ba as a proxy to
99 estimate local processes of POC remineralization in the Mediterranean Sea.

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101 **2. Experiment and methods**

102 **2.1 Study area**

103 The whole water column was sampled for D_Ba along an east to west
104 transect across the Mediterranean Sea from off the coast of Lebanon to the Strait
105 of Gibraltar, enabling creation of a quasi-zonal section (M84/3 cruise, Istanbul to
106 Vigo, 5-28 April 2011, R/V *Meteor*) (Figure 1) (Tanhua et al., 2013a). However,
107 the Sicily Channel could not be sampled due to political instability in the region.
108 Additionally, we present a short meridional section from the Adriatic Sea through
109 the Strait of Otranto to the Ionian Sea (later referred to as the Ionian section). The
110 period of the M84/3 cruise, April 2011, coincides with the end of the winter-
111 spring bloom. The cruise was set up to follow the guide-lines of the GO-SHIP
112 Program (Global Ocean Ship Based Hydrographic Investigation Program), which
113 aims at creating a globally coordinated network of sustained hydrographic
114 sections as part of the global ocean/climate observing system. The principal
115 scientific objective for M84/3 was to understand and document large-scale
116 Mediterranean water property distributions, their changes and the drivers of those
117 changes. In particular, M84/3 focused on major shifts in the overturning

118 circulation of the Mediterranean basin which began at the end of the 1980s for the
119 EMed (Roether et al., 1996) and in the mid-2000s for the WMed (Schroeder et al.,
120 2008). Our specific objective was to document for the first time the D_Ba
121 distribution in the Mediterranean basin at a large scale. D_Ba data are available in
122 the CDIAC (Carbon Dioxide Information Analysis center) data repository, next to
123 other physical and chemical parameters obtained during the M84/3 cruise
124 (http://cdiac.ornl.gov/oceans/Coastal/Meteor_Med_Sea.html).

125 Detailed description of the Mediterranean circulation as well as water mass
126 properties and distribution is given in Tanhua et al. (2013b) and Hainbucher et al.
127 (2014). Briefly, the following main water masses can be distinguished (see
128 potential temperature – salinity diagram in Fig.2; note that the mesopelagic layer
129 is hereafter referred to as the intermediate layer): (1) the western part of the zonal
130 section is dominated by the inflow of surface Atlantic Water (AW) associated
131 with an intense meso-scale activity along the African coast, and the outflow of
132 Mediterranean Overflow Water (MOW). AW is mainly detected by fresher
133 waters; (2) from west to east, AW is gradually replaced by Ionian Surface Water
134 (ISW) and Levantine Surface Water (LSW). LSW is formed by intensive heating
135 and evaporation and has the highest salinity and temperature of the entire
136 MedSea; (3) Levantine Intermediate Water (LIW) is present at intermediate layers
137 over the whole basin and represents the intermediate water mass connection
138 between sub-basins. LIW is characterized by high density and a salinity
139 maximum. During the M84/3 cruise, the core of LIW was detected around 200 m
140 depth in the EMed and around 500 m depth in the WMed. Cretan Intermediate
141 Water (CIW) is also found at intermediate depths in the EMed; (4) in the deep
142 waters we find Eastern Mediterranean Deep Water (EMDW) and Western

143 Mediterranean Deep Water (WMDW), in each sub-basin. EMDW is a mixture of
144 Adriatic Deep Water (AddW), Cretan Deep Water (CDW) and shallower water
145 masses. WMDW is mainly formed in the Gulf of Lion by open-ocean convection
146 (Schott et al., 1996) with intermittent contribution from shelf water cascading
147 (Durrieu de Madron et al., 2013).

149 **2.2 Sampling and analyses**

150 Seawater was sampled with a CTD rosette equipped with 24 12-liter water
151 bottles. Then, fifteen mL of unfiltered seawater were collected in pre-cleaned
152 polypropylene bottles (Nalgene; rinsed three times with the same seawater
153 sample), acidified with 15 μL of HCl (Optima grade) and kept at room
154 temperature for later analysis. No filtration of the seawater was done based on the
155 well-documented knowledge that D_Ba represents, in general, a very large
156 fraction (>99%) of total Ba. There were 47 vertical D_Ba profiles with a total of
157 833 D_Ba samples.

158 D_Ba was measured using an isotope dilution (ID) method (Klinkhammer
159 and Chan, 1990 and Freydier et al., 1995) by high resolution sector field -
160 inductively coupled plasma- mass spectrometry (SF-ICP-MS). This method was
161 adapted to a Thermo Finnigan Element XR instrument. The D_Ba measurements
162 presented here are the sum of dissolved Ba (D_Ba) and a very small fraction
163 (generally <1% of total Ba) that is generated from the particulate Ba pool as a
164 result of the acidification. For the sake of simplicity, we use the term of D_Ba.
165 Samples (0.5 mL) were spiked with 300 μL of a ^{135}Ba -enriched solution (93%
166 ^{135}Ba ; 95 nmol kg^{-1}), and 300 μL of a Nd solution (natural isotopic composition;
167 70 nmol kg^{-1}) was added as an internal standard to correct for mass bias. Finally,

168 samples were diluted with 15 mL of acidified (2% HNO₃, Optima grade) Milli-Q
169 grade water. The amount of sample, spikes and dilution water were assessed by
170 weighing. Reproducibility of this method is 1.5% (RSD) as tested on repeated
171 preparations of reference solutions: SLRS-5 (NRC-CNRC river water reference
172 material for trace metals; 101.9 ± 3.6 nmol kg⁻¹) and a house-made reference of
173 Mediterranean Sea water (deep water from the MOOSE DYFAMED site; 54.1
174 nmol kg⁻¹). The limit of detection, calculated as three times the standard deviation
175 of the procedural blank, is 0.09 nmol kg⁻¹.

176 Using the D_Ba concentration, temperature, pressure and salinity data
177 from the M84/3 cruise, we calculated the barite saturation index (SI) following the
178 procedures described by Monnin et al. (1999) and Monnin and Cividini (2006). SI
179 is defined as the Q/K ratio, where Q is the ionic product of aqueous barium
180 sulphate, and K is the solubility product of barite. A saturation index value
181 between 0.9 and 1.1 is taken to represent equilibrium (Monnin et al., 1999).
182 Waters are considered to be undersaturated for SI <0.9.

184 3. RESULTS

185 Figure 3 shows the full-depth D_Ba distribution for the Ionian and zonal
186 sections, with the top 500 m expanded. The same scheme is reported for the barite
187 saturation index (SI) in Figure 4. Figure 5 shows characteristic vertical D_Ba
188 profiles for the major sub-basins, as well as D_Ba profiles for stations not
189 included in the Ionian and zonal sections. Two broad features characterize the
190 D_Ba in the Mediterranean Sea: 1) a vertical gradient increasing from 38 nmol kg⁻¹
191 near the surface to 85 nmol kg⁻¹ at the bottom, with local deep D_Ba maxima
192 reaching up to 172 nmol kg⁻¹, and 2) a pronounced water column undersaturation

193 with respect to barite ($0.2 \leq SI \leq 0.6$) with a relative maximum in the intermediate
194 waters at around 500 meters depth.

195 West of Gibraltar, in the Gulf of Cadiz, D_Ba concentrations range from
196 38 to 55 nmol kg⁻¹ in highly undersaturated waters (SI from 0.2 to 0.4) with only
197 small vertical gradients (see representative D_Ba profile at station #340 in Figure
198 5a). The low D_Ba and SI characteristic of AW can be followed throughout the
199 surface waters of the Mediterranean Sea. For the upper 1000 m in the WMed, the
200 D_Ba distribution is marked by increasing D_Ba concentration <70 nmol kg⁻¹
201 from west to east. In the EMed, the intermediate layer (200 to 700 m depth) is
202 marked by slightly lower D_Ba concentration (50 to 70 nmol kg⁻¹) between 17
203 and 26°E.

204 The deep (>1000 m) layers of the Mediterranean Sea are characterized by
205 D_Ba concentrations above 70 nmol kg⁻¹ with localized patches peaking up to 100
206 nmol kg⁻¹. Those are observed at 9.4°E in the WMed (station #321) and at 27.5°E
207 in the EMed (station # 290) (see D_Ba profiles in Figure 5f). Very high D_Ba
208 concentrations (139 and 172 nM, respectively) are furthermore found near the
209 bottom at 33°E (station #291) and 21.5°E (station #301) (see D_Ba profiles in
210 Figure 5g). Note that very high D_Ba contents (up to 160 nmol kg⁻¹) are also
211 found near the bottom at station #288 located at 26.2°E north-east of Crete (not
212 shown in the zonal section; see D_Ba profile in Figure 5g).

213 The same general features as reported for the zonal section are observed
214 across the Ionian section, where the D_Ba distribution is also marked by an
215 increase in the water column D_Ba content (from 48 to 95 nmol kg⁻¹) in
216 undersaturated waters (SI from 0.3 to 0.5). A SI maximum again extends in
217 intermediate waters and lower D_Ba concentrations (<70 nmol kg⁻¹) occur

1 218 between 500 and 800 m along the Ionian section. The northern part of the Ionian
2 219 section, north of the Otranto Strait (Adriatic Pit), is marked by relatively
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4 220 homogeneous D_Ba concentrations ($<65 \text{ nmol kg}^{-1}$) below 300 m (see D_Ba
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7 221 profile at station #313 in Figure 5c). Also, a particular D_Ba increase (up to 95
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9 222 nmol L^{-1}) is observed around a depth of 2000 m (station #307; see D_Ba profile in
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12 223 Figure 5c). Note that a similar increase in D_Ba concentrations around the same
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14 224 depth is detected at station #314 located in the area of station #307 (not shown in
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17 225 Fig.3; see D_Ba profile in Figure 5c). D_Ba increase around a depth of 2000 m is
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19 226 also observed in the EMed at stations #303 (southern Ionian Sea) and at stations
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21 227 #300 (24.3°E) and #298 (22.5°E) (not shown in Fig.3; see D_Ba profiles in Figure
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28 230 **4. DISCUSSION**

31 231 D_Ba concentrations reported in the present work (from 38 to 100 nmol
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33 232 kg^{-1}) are of the same order of magnitude as D_Ba values reported during previous
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36 233 Mediterranean cruises in the EMed (GEODYME data, Jeandel et al., pers. comm.)
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38 234 and in the WMed (Bernat et al., 1972; Dehairs et al., 1987; van Beek et al., 2009).
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41 235 Previous MedSea data are however relatively scarce, with in general limited
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43 236 vertical sampling resolution, preventing direct comparisons with the present data
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46 237 set. D_Ba concentrations for the MedSea are also of the same order of magnitude
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48 238 as values reported for the Atlantic sector (Chan et al., 1977), the Indian and
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51 239 Southern Oceans (Jeandel et al., 1996; Jacquet et al., 2004, 2007, Hoppema et al.,
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53 240 2010) and for the North Pacific (Dehairs et al., 2008). Compared to the previous
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56 241 sectors, D_Ba concentrations in the MedSea present however smaller vertical
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58 242 D_Ba gradients which mainly range from 38 to 85 nmol kg^{-1} between the surface
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243 and the bottom. Our results indicate that the MedSea is undersaturated with
244 respect to barite everywhere, in contrast to the above-mentioned oceans where
245 saturation can be reached at certain locations (Monnin et al., 1999; Dehairs et al.,
246 2008; Jacquet et al., 2008). SI exhibits a maximum value at depths around 500 m.
247 Below these depths, the variations in D_Ba concentration and temperature are
248 small. The only factor affecting the SI value is pressure. The increase with
249 pressure of the barite solubility product (K) is much larger than the increase of the
250 aqueous barium sulphate ionic product (Q) which is proportional to the square of
251 the activity coefficient of aqueous barium sulphate (Monnin et al., 1999; Monnin
252 and Cividini, 2006). This results in a decrease of the barite SI with depth at depth
253 ranges where D_Ba and temperature are almost constant (i.e. the variations are too
254 low to affect SI).

255 For the upper 1000 m, the general zonal D_Ba pattern appears influenced
256 by the water circulation in the Mediterranean basin. In the western part of the
257 transect, the low D_Ba contents and SI values coincide with the low-salinity
258 surface AW flowing through the Strait of Gibraltar. The transition between AW
259 and underlying LIW (referred to as MOW in the Gibraltar Strait) is marked by a
260 steep vertical D_Ba gradient (D_Ba concentrations from <55 to >70 nmol kg⁻¹). In
261 the northern part of the Ionian section, the relatively homogeneous D_Ba
262 concentrations (at values <65 nmol kg⁻¹) below 300 m result from the transition
263 above the Otranto Strait from northward progressing LIW to less salty Adriatic
264 waters potentially influenced by riverine input. Between 17 and 26°E in the
265 EMed, low D_Ba values (D_Ba contents from 50 to 70 nmol kg⁻¹) coincide in the
266 upper 400 m with the sinking and westward progression of high density LIW
267 (salinity maximum between 200 and 500 m). The sinking of isolines from east to

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268 west in this zone is a feature also observed for other water mass properties
269 (salinity, temperature, potential density and nutrients) (Tanhua et al., 2013b). It is
270 furthermore possible that the extent of lower D_Ba concentrations down to 700 m
271 in this area reflects D_Ba subtraction due to P_Ba barite formation. The same is
272 true for the lower D_Ba concentrations reported along the Ionian section between
273 500 and 800 m.

274 Concerning the deeper (>1000 m) water column, the high values of D_Ba
275 reported at 9.4°E and 27.5°E (up to 100 nmol kg⁻¹) coincide with the top of
276 seamounts. This Ba enrichment may be due to local dissolution of Ba-rich
277 particles (barite) in the under-saturated water and would reflect epibenthic fluxes
278 of Ba-rich particles that have been exported from the intermediate layers to the sea
279 floor. This may also occur at station #291 (33°E) where the high D_Ba value of
280 139 nmol kg⁻¹ is found near the seafloor. The same is true for station #288 (north-
281 east of Crete) where D_Ba concentrations near the seafloor reach 160 nmol kg⁻¹.
282 Another source of very high D_Ba concentrations in the MedSea could originate
283 from the Black Sea where Moore and Falkner (1999) reported water column
284 D_Ba concentrations ranging from 130 to 500 nmol kg⁻¹. No particularly high
285 water column D_Ba concentration is however reported at station #287 in the
286 southern Eagean Sea, nor further south at station #289 located in the area of
287 station #288 north-east of Crete (Fig.5e). A particular situation is also encountered
288 at 21.5°E (station #301) where the highest D_Ba concentration (172 nmol kg⁻¹) of
289 the whole dataset is found close to the “Atalante” brine lake, a water body with
290 very high salinity (up to 160) and anoxic conditions. It has been well established
291 that brines are highly concentrated in various elements (e.g. trace metals).
292 Extremely high D_Ba contents (up 670 nmol kg⁻¹) resulting from sulphate salt

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293 dissolution have for instance been reported in the Orca basin (Gulf of Mexico)
294 (Schijf, 2007). The high D_Ba contents reported at 21.5°E (station #301) in the
295 EMed do not therefore reflect a higher export of Ba-rich particles to the seafloor,
296 benthic processes, nor a possible influence of Black Sea waters, but rather an
297 influence of the nearby brine lake.

298 The observed D_Ba variation with depth (surface depletion and depth
299 enrichment) is often referred to as a nutrient-like distribution. The precise
300 mechanism shaping this D_Ba distribution is still debated mainly because the
301 control on barite formation inside POC micro-environments in undersaturated
302 ocean waters is not fully resolved (Griffith and Paytan, 2012). The nutrient
303 distribution during M84/3 (late winter-spring) is characterized by very low
304 concentrations, in particular in the EMed (Tanhua et al., 2013b). The same trend
305 was reported in previous studies emphasizing the increasing oligotrophic trend
306 from west to east along the basin (Moutin and Raimbault, 2002; Pujo-Pay et al.,
307 2011). The D_Ba distribution is more uniform between WMed and EMed during
308 M84/3 than reported for nutrients (Tanhua et al., 2013b). Also, the D_Ba
309 distribution is not fully depleted in surface waters and presents specific local
310 depletions at intermediate depths. Jeandel et al. (1996) and Jacquet et al. (2007)
311 reported a decoupling between D_Ba and silicate and alkalinity distributions in
312 the water column due to the fact that D_Ba is not controlled by the same
313 biogeochemical processes as those controlling the synthesis of opal and carbonate,
314 and their dissolution. Throughout the whole basin, while barite is undersaturated,
315 calcite and aragonite are largely supersaturated (Alvarez et al., 2014). This would
316 explain decoupling between D_Ba and total alkalinity in the deep waters (not
317 shown; see Alvarez et al., 2014), as reflected by increasing D_Ba concentrations

despite constant total alkalinity in the water column below 1000 m, especially in the EMed. The D_Ba enrichment in deep waters reflects dissolution of Ba-rich particles produced at intermediate depths and exported to the sea floor. This D_Ba increase may be enhanced by the residence time and ventilation of deep waters. Studies of transient tracers (CFC-12, SF₆ and tritium) over the last two decades revealed a period of low ventilation in the deep eastern (Levantine) basin, while the WMed was marked by massive input of recently ventilated water (Ströven and Tanhua, 2013; Schneider et al., 2014; Schröder et al., 2008, 2010). These differences in the ventilation of deep water masses could explain the fact that the extent of high D_Ba values is larger in the EMed than in the WMed. Nevertheless, the fact that over the basin the D_Ba concentration increases with depth indicates dissolution of Ba-rich particles produced at intermediate depths during POC remineralization processes and transferred through the deep water. Our results indicate that this transfer of Ba-rich particles is more important at 9°E in the WMed and east of 25°E in the EMed (i.e. D_Ba contents >80 nmol kg⁻¹). The particulate and dissolved organic carbon (POC, DOC) dynamics in the MedSea are relatively complex (Lefèvre et al., 1996; Santinelli et al., 2010; Lopez-Sandoval et al., 2011; Luna et al., 2012). It is therefore difficult to discuss in detail the link between the deep water column transfer of Ba-enriched particles and sinking POC.

338

339 5. CONCLUSION

340 The present paper presents an extended data set on the D_Ba distribution
341 along a high resolution and quasi-zonal transect in the MedSea in late winter-
342 spring 2011. Our results reveal that the D_Ba distribution appears driven by

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343 hydrodynamics, while enhanced D_Ba contents in deep waters could reflect the
344 effect of a higher P_Ba barite flux in undersaturated water. Also, the occurrence
345 of lower D_Ba contents at intermediate depths could reflect horizons of intense
346 particulate and dissolved Ba dynamics. In order to further constrain the link
347 between these specific features of the D_Ba distribution and the organic carbon
348 dynamics in the MedSea, the sensitivity of the Ba signal to the phytoplankton
349 growth season and to dense-water formation events should be addressed.

350

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366

367 **Figure captions**

368

369 Figure 1: Map of the Mediterranean Sea with the stations (blue dots) of the M84/3
370 cruise where samples were taken for the analysis of dissolved barium, along with
371 the bathymetry of the basins. WMED: Western Mediterranean Sea, EMED:
372 Eastern Mediterranean Sea. Figure constructed using Ocean Data View (Schlitzer,
373 2003).

374

375 Figure 2: Potential temperature – salinity diagram with isopycnals (kg m^{-3}) of the
376 whole data set (a) and focus on deep waters (b). Colors represent the
377 concentration of D_Ba in nmol kg^{-1} . WMed, EMed: Western and Eastern
378 Mediterranean Sea. AW= Atlantic Water, MOW= Mediterranean Overflow
379 Water, ISW= Ionian Surface Water, LSW= Levantine Surface Water, LIW=
380 Levantine Intermediate Water, CIW= Cretan Intermediate Water, WMDW=
381 Western Mediterranean Deep Water, AdDW= Adriatic Deep Water, CDW=
382 Cretan Deep Water.

383

384 Figure 3: Sections of D_Ba distribution (nmol kg^{-1}) in the Mediterranean Sea from
385 the Meteor cruise M84/3 (April 2011). The top-right panel is a meridional section
386 from the Adriatic Sea to the Ionian sea (light grey line on the map) and the lower
387 panel is the zonal section from the coast of Lebanon in the EMed to the Strait of
388 Gibraltar in the WMed (dark grey line on the map). The depth scale and the color
389 scale are identical for all panels. The top 500 m in each section and associated
390 color scale are slightly expanded.

391

392 Figure 4: Similar to Fig.3, but for barite saturation index (SI).

393

394 Figure 5: Characteristic vertical D_Ba profiles for the major sub-basins and D_Ba
395 profiles for stations not included in the Ionian and zonal sections.

396

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Figure2

Figure3

Figure4

Figure5

D_Ba is investigated along a high resolution and quasi-zonal transect in the MedSea.

The D_Ba content ranges from 38 to 85 nmol kg⁻¹ with local deep D_Ba maxima reaching up to 172 nmol kg⁻¹

The water column is largely undersaturated with respect to barite ($0.2 < SI < 0.6$).

The D_Ba distribution is impacted by the large-scale Mediterranean circulation and biogeochemical processes.

Local changes in the D_Ba patterns may be key to better constrain the C dynamics in the MedSea.