



1	On the barium - oxygen consumption relationship in the Mediterranean Sea: implications
2	for mesopelagic marine snow remineralisation.
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18 ABSTRACT

In the ocean, remineralisation rate associated with sinking particles is a crucial variable. Since 19 the 90's, particulate biogenic barium (Baxs) has been used as an indicator of carbon 20 21 remineralization by applying a transfer function relating Ba_{xx} to O_2 consumption (Dehairs's transfer function, Southern Ocean-based). Here, we tested its validity in the Mediterranean Sea 22 (ANTARES / EMSO-LO) for the first time by investigating connections between Baxs, 23 24 prokaryotic heterotrophic production (PHP) and oxygen consumption (JO₂-Opt; optodes measurement). We show that: (1) higher Baxs (409 pM; 100- 500 m) in situations where 25 integrated PHP (PHP100/500= 0.90) is located deeper, (2) higher Ba_{xx} with increasing JO₂-Opt, 26 and (3) similar magnitude between JO₂-Opt (3.14 mmol m⁻² d⁻¹; 175- 450 m) and JO₂-Ba (4.59 27 mmol m⁻² d⁻¹; transfer function). Overall, Ba_{xs}, PHP and JO₂ relationships follow trends observed 28 in the Southern Ocean. We believe that such transfer function could apply in the Mediterranean 29 Sea with no restriction. 30

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KEY WORDS: particulate biogenic barium, mesopelagic zone, oxygen consumption,
 prokaryotic heterotrophic production, carbon remineralization, Mediterranean Sea





36 1. INTRODUCTION

Ocean ecosystems play a critical role in the Earth's carbon (C) cycle [IPCC, 2014]. The 37 38 quantification of their impacts of both present conditions and future predictions remains one of 39 the greatest challenges in oceanography [Siegel et al., 2016]. In essence, the biological C pump is termed for the numerous processes involved in maintaining the vertical gradient in dissolved 40 inorganic C. This includes processes such as organic matter production in surface, its export and 41 42 subsequent remineralization. Most of marine snow organic C conversion (i.e. remineralization) into CO_2 by heterotrophic organisms (i.e. respiration) occurs in the mesopelagic zone (100-1000 43 m) [Martin et al., 1987; Buesseler and Boyd, 2009]. Globally, the flux of C exported below 1000 44 45 m depth is the key determinant of ocean carbon storage capacity [Henson et al., 2011]. However, there is no consensus on C transfer efficiency estimations from field experiments, leading to an 46 imbalance of the water column C budget [Giering et al., 2014]. Resolving this imbalance is in the 47 core of numerous studies in the global ocean, but also regionally, especially in the Mediterranean 48 Sea (MedSea). Due to limited exchanges with adjacent basin and the existence of an intense 49 overturning circulation qualitatively resembling the global one (but with shorter time scales), the 50 51 MedSea is often considered as a laboratory to observe and understand the impact of transient climate variability on ecosystems and biogeochemical cycles [Malanotte-Rissoli et al., 2014]. In a 52 context of climate changes, better constraining C fluxes and the ocean C storage capacity is of 53 54 crucial importance.

Particulate barium in excess (Ba_{xs} , i.e. biogenic Ba from total particulate Ba after correction for lithogenic Ba) is a geochemical tracer of particulate organic carbon (POC) remineralization in the mesopelagic layer [Dehairs et al., 1997]. Ba_{xs} mostly occurs in the form of barite microcrystals (BaSO₄) at these depths. In a global ocean undersaturated with respect to barite, studies report that Ba_{xs} would precipitate inside oversaturated biogenic micro-environments during POC





degradation by heterotrophic prokaryotes in the mesopelagic zone, through sulfate and/or barium 60 enrichment [Bertram and Cowen, 1997]. The first-ever studies on mesopelagic Baxs reported 61 coinciding Baxs maxima with depths of dissolved O₂ minimum and pCO₂ maximum [Dehairs et 62 al., 1987, 1997]. By using an 1D advection-diffusion model applied to highly resolved, precise 63 O₂ profiles in the Atlantic sector of the Southern Ocean (ANTX/6 cruise; Shopova et al., 1995), 64 Dehairs et al. [1997] established an algorithm converting mesopelagic Ba_{xs} concentration into O_2 65 consumption rate (JO₂) and organic C remineralized (POC remineralization rate). This transfer 66 function has been widely used until now [Cardinal et al., 2001- Lemaitre et al., 2018]. Yet its 67 validity has never been tested in other oceanic provinces. Recently, significant progresses were 68 made in relating Ba_{xx} , O_2 dynamics to prokaryotic heterotrophic activity [Jacquet et al., 2015]. 69 Nevertheless, the Dehairs transfer function has never been revised since. These advancements 70 clearly show that Baxs is closely related with the vertical distribution of prokaryotes heterotrophic 71 72 production (PHP) (the rate of change with depth), reflecting the temporal progression of POC remineralization processes. Also, in a first attempt to test the validity of the Dehairs's transfer 73 function in other locations, Jacquet et al. [2015] confronted oxygen consumption rates (JO₂) from 74 75 direct measurements (dark community respiration, DCR) to derived JO₂ from Ba_{xs} data (using the transfer function) in the Kerguelen area (Indian sector of the Southern Ocean). We revealed good 76 convergence of JO_2 rates from these two approaches, further supporting the Dehairs's function to 77 78 estimate POC remineralization rates in different biogeochemical settings of the Southern Ocean.

Here, we further investigate relationships between the mesopelagic Ba_{xs} proxy, prokaryotic activity and oxygen dynamics (Figure 1a) in the northwestern Mediterreanean Sea (MedSea), a different biogeochemical setting to those already studied (see references above). Today, observations of the various components of the MedSea biological C pump provide organic C fluxes varying by at least an order of magnitude [Santinelli et al., 2010; Ramondenc et al., 2016].





Malanotte-Rissoli et al. [2014] reviewing unsolved issues and future directions for MedSea 84 research highlighted the need to further investigate biogeochemical processes at intermediate 85 86 (mesopelagic) and deep layers to reconciliate the C budget in the Mediterranean basin. Previous 87 particulate Baxs dataset is very scarce in the NW- MedSea, with in general very low vertical sampling resolution [Sanchez Vidal et al., 2005] or very restricted studied areas [Dehairs et al., 88 1987; Sternberg et al., 2008]. Here we discuss Ba_{xs} , PHP and JO₂ (from optodes measurement 89 90 during incubations) at the ANTARES / EMSO-LO observatory site (Figure 1a, b). We hypothesize that the Dehairs's transfer function converting Baxs into POC remineralization also 91 applies in a different ocean ecosystem functioning from the Southern Ocean. We suggest that the 92 93 Baxs proxy can be used as routine tracer to estimate local-scale processes of mesopelagic POC 94 remineralization in the Mediterranean basin.

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96 2. SAMPLING AND ANALYSES

97 **2.1 STUDY SITE**

The BATMAN cruise (https://doi.org/10.17600/16011100, March 10-16 2016, R/V EUROPE) 98 99 took place to the ANTARES / EMSO-LO observatory site (42°48'N, 6°10'E; Tamburini et al., 2013), 40 km off the coast of Toulon, southern France (Figure 1b). The hydrological and 100 biogeochemical conditions at this site are monitored monthly in the framework of the MOOSE 101 102 (Mediterranean Ocean Observing System for the Environment) program and of the EMSO (European Multidisciplinary Subsea Observatory) observation program. The hydrography 103 displays the general three-layer MedSea system with surface, intermediate and deep waters 104 105 [Hainbucher et al., 2014]. Briefly, the main water masses can be distinguished (see potential temperature - salinity diagram during the BATMAN cruise in Figure 1c): (1) Surface Water 106 107 (SW); (2) Winter Intermediate Water (WIW) and Levantine Intermediate water (LIW). LIW is





present at intermediate depths (around 400 m at ANTARES) and is characterized by temperature

and a salinity maxima; (4) Mediterranean Deep Water (MDW).

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111 2.2 ANALYSES

112 For particulate barium, 4 to 7 L of seawater sampled using Niskin bottles were filtered onto 47 mm polycarbonate membranes (0.4 µm porosity) under slight overpressure supplied by filtered 113 114 air. Filters were rinsed with few mL of Milli-Q grade water to remove sea salt, dried (50°C) and stored in Petri dishes. Thirteen depths between surface and 2000 m were sampled by combining 115 different casts sampled closeby in time and space (total of 28 samples). In the laboratory, we 116 performed a total digestion of filters using a tri-acid (0.5 mL HF /1.5 mL HNO₃ / HCl 1 mL; all 117 Optima grade) mixture in closed teflon beakers overnight at 95°C in a clean pressurized room. 118 After evaporation close to dryness, samples were re-dissolved into 10 mL of HNO₃ 2%. The 119 solutions were analysed for Ba and other elements of interest (Na and Al) by HR-ICP-MS (High 120 Resolution-Inductively Coupled Plasma- Mass Spectrometry; ELEMENT XR ThermoFisher). 121 Details on sample processing and analysis are given in Cardinal et al. [2001] and Jacquet et al. 122 123 [2015]. The presence of sea-salt was checked by analysing Na and the sea-salt particulate Ba contribution was found negligible. Particulate biogenic barium in excess (hereafter referred to as 124 Ba_{xs}) was calculated as the difference between total Ba and lithogenic Ba using Al as the 125 126 lithogenic reference element [Taylor and Mc.Lennan, 1985]. The standard uncertainty [Ellison et al., 2000] on Baxs concentration ranges between 5.0 and 5.5%. The term "in excess" is used to 127 indicate that concentrations are larger than the Baxs background. The background (or residual 128 value) is considered as "preformed" Baxs at zero oxygen consumption left over after transfer and 129 partial dissolution of Baxs produced during degradation of previous phytoplankton growth events. 130





131	Oxygen concentrations were measured using optical oxygen sensor (Aanderaa 4330-Optodes)
132	at 4 depths in the mesopelagic layer (175, 250, 450 and 1000 m). In total each of the 8 optodes
133	(two per depths) were placed into a sealed 1L borosilicate glass bottles incubated at a fixed
134	temperature of 13°C in thermo-regulated baths for 24 to 48 hours. Oxygen consumption rates
135	(later referred to as JO2-Opt) were calculated from oxygen concentration evolution with time
136	applying linear model calculations.

Prokaryotic heterotrophic production (PHP) estimation was measured over time course experiments at *in situ* temperature (13°C) following the protocol described in Tamburini et al. [2002]. ³H-leucine labelled tracer [Kirchman, 1993] was used. To calculate prokaryotic heterotrophic production, we used the empirical conversion factor of 1.55 ng C per pmol of incorporated leucine according to Simon and Azam [1989], assuming that isotope dilution was negligible under these saturating concentrations.

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144 **3. RESULTS AND DISCUSSION**

145 **3.1 Barium vertical distribution**

146 Particulate biogenic Ba_{xs}, particulate Al (pAl) and biogenic Ba fraction profiles in the upper 1000 m at ANTARES are reported in Figure 2a. Baxs concentrations range from 12 to 719 pM. 147 The biogenic Ba fraction range from 51 to 91 % of the total particulate Ba signal. Particulate Al 148 149 concentrations (pAl) are low and range from 8 to 170 nM. Baxs concentrations are low in surface water (<100 pM) where the lithogenic fraction reaches 43 to 49 % in the upper 70 m. From 150 previous studies we know that Baxs in surface waters is distributed over different, mainly non-151 152 barite biogenic phases, and incorporated into or adsorbed onto phytoplankton material. As such these do not reflect POC remineralization processes, in contrast to mesopelagic waters where 153 154 Baxs is mainly composed of barite formed during prokaryotic degradation of organic matter. At





ANTARES the Baxs profile displays a mesopelagic Baxs maximum between 100 and 500 m, 155 reaching up to 719 pM at 175 m. Ba is mostly biogenic at these depths (> 80 %). Ba_{xs} 156 concentrations then decrease below 500 m to reach a background value of around 130 pM (see 157 BKG in Figure 2). Note that the MedSea is largely undersaturated with respect to barite, with 158 saturation state ranging between 0.2 and 0.6 over the basin [Jacquet et al., 2016; Jullion et al., 159 2017]. For comparison, the Ba background value in the Southern Ocean reaches 180 to 200 pM 160 161 below 1000 m [Dehairs et al., 1997; Jacquet et al. 2015]. Previously, Sternberg et al. [2008] reported the seasonal evolution of Baxs profiles at the DYFAMED station (43°25'N-7°52'E; 162 BARMED project) northeast from ANTARES (Figure 1c) in the NW-MedSea. The present Baxs 163 profile at ANTARES (March 2016) is very similar to the Baxs profile measured in March 2003 at 164 DYFAMED (Figure 2a). The slight difference between Baxs profiles in the upper 75 m suggests 165 more Ba bounded and/or adsorbed onto phytoplankton material during BARMED. Both profiles 166 present a Baxs maximum in the upper mesopelagic zone between 150 and 200 m. Below this 167 maximum, Baxs concentrations gradually decrease to reach around 130 pM between 500 and 168 1000 m (this study). A similar value was reached between 500 and 600 m at the DYFAMED 169 170 station over the whole studied period (between February and June 2003; Sternberg et al., 2008).

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172 **3.2 Prokaryotic heterotrophic production**

The particulate excess Ba (>BKG) is centred in the upper mesopelagic zone between 100 and 500 m and reflects that POC remineralization mainly occurred at these depths (Figure 2a). Depthweighted average (DWA) Ba_{xs} content (409 pM) was calculated over this entire depth interval. Figure 2b shows column-integrated PHP at 100 m over column-integrated PHP at 500 m (PHP100/500= 0.90), according to the relationship obtained during KEOPS1 (summer) and KEOPS2 (spring; out plateau stations) cruises in the Southern Ocean [Jacquet et al., 2008; 2015]





and #DY032 cruise (2015, R/V DISCOVERY) at the PAP (Porcupine Abyssal Plain) observatory 179 in the northeast Atlantic (49°N, 16.5 °W) (personal data). Results at the ANTARES / EMSO-LO 180 181 site follow the trend previously reported in the Southern Ocean, indicating higher DWA Baxs in 182 situations where a significant part of column-integrated PHP is located deeper in the water column (high Int. PHPx1/IntPHPx2 ratio; Figure 2b). These previous studies revealed that the 183 shape of the column-integrated PHP profile (i.e. the attenuation gradient) is important in setting 184 185 the Baxs signal in the mesopelagic zone (Dehairs et al., 2008; Jacquet et al., 2008, 2015]. Indeed, mesopelagic Baxs appears reduced when most of the column-integrated PHP is limited to the 186 upper layer (indicating an efficient remineralization in surface), compared to situations where a 187 significant part of integrated PHP is located deeper in the water column (reflecting significant 188 deep PHP activity, POC export and subsequent remineralization) (Figure 2b). Our MedSea 189 results are located along the trend defined in the Southern Ocean during KEOPS1 cruise. It is 190 generally considered that Baxs (barite) forms inside sulfate and/or barium oversaturated biogenic 191 micro-environments during POC degradation by heterotrophic prokaryotes. However, it is 192 unclear whether barite formation at mesopelagic depths is (directly or indirectly) bacterially 193 194 induced or bacterially influenced. Overall, our results strengthen the close link between the water column Ba_{xs} distribution and respiration (organic matter degradation). 195

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197 3.3 Oxygen- barium relationship

The relationship we obtained at ANTARES between Ba_{xs} concentrations and oxygen consumption rates from optodes measurements (JO₂-Opt) is reported in Figure 3a. JO₂-Opt range from 0.11 to 5.85 µmol L⁻¹ d⁻¹. The relationship indicates higher Ba_{xs} concentrations with increasing JO₂-Opt. An interesting feature is the intercept at zero JO₂-Opt (around 128 pM)





which further supports the Ba BKG value at ANTARES (130 pM) determined from measured

203 Ba_{xs} profiles (Figure 3a).

We applied a similar approach as reported in Jacquet et al. (2015) where we show the correlation between JO₂ obtained from dark community respiration DCR (winkler titration; JO₂-DCR) data integration in the water column and JO₂ based on Ba_{xs} content (Dehairs's transfer function; later referred to as JO₂-Ba). Similarly, to estimate JO₂-Ba in the present study we used the following equation [Dehairs et al., 1997]:

 $JO_2-Ba = (Ba_{xs} - Ba BKG)/17450$ (1)

A Ba BKG value of 130 pM was used (see above). JO₂-Ba is confronted to JO₂-Opt integrated 210 211 over the same layer depth (between 175 and 450 m; Figure 3b). JO_2 rates are of the same order of magnitude (JO₂-Ba= 4.59 mmol m⁻² d⁻¹ and JO₂-opt= 3.14 mmol m⁻² d⁻¹). The slight difference 212 could be explained by the integration time of both methods: few hours to days for the incubations 213 214 vs. few days to weeks for Ba_{xs} (seasonal build-up; Jacquet et al., 2007). JO₂ rates calculated in the present work are 3 times higher than those reported in the Southern Ocean during KEOPS1 215 [Jacquet et al., 2015] but they are in good agreement with the Baxs vs JO₂ trend (Figure 3b). 216 217 Overall, our results indicate similar Ba_{xs} - JO_2 relationship in the Southern Ocean and the Mediterranean Sea. This further supports the universal validity of the Dehairs's transfer function 218 in the present study. 219

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221 **3.4 Estimated particles remineralisation rates and implications**

In order to provide a Ba_{xs} -derived estimate of POC remineralization rate (MR) at the ANTARES / EMSO-LO observatory during BATMAN cruise, we converted JO₂-Ba into C respired using the Redfield (RR) C/O₂ molar ratio (127/175; Broecker et al., 1985) multiplied by the depth layer considered (Z) [Dehairs et al., 1997]:





 $MR = Z \times JO_2 - Ba \times RR \quad (2)$

We obtain a POC remineralization rate of 11 mmol C $m^{-2} d^{-1}$ (10% RSD). This is within the range of previously published remineralization fluxes in the Mediterranean Sea from sediment trap [Sanchez-Vidal et al., 2005] and from thorium-derived data [Speicher et al., 2006]. It is also in good agreement with recent POC flux attenuation combining drifting sediment traps and underwater vision profilers [Ramondenc et al., 2016].

232 The present paper brings a first insight into the connections of Ba_{xs} , PHP and JO_2 at the ANTARES/EMSO-LO observatory site in the northwestern Mediterranean Sea during the 233 BATMAN (2016) cruise. Our results reveal a strong relationship between Baxs contents and 234 235 measured JO₂ rates. Also, DWA Baxs vs. column integrated PHP, as well as measured vs. Baxsbased JO₂ relationships follow trends previously reported in the Southern Ocean where the 236 Dehairs's function was first established to estimate POC remineralisation rate. Results from the 237 present study would indicate that this function can also be applied in the Mediterranean basin 238 provided that adequate Baxs background values are estimated. From a global climate perspective, 239 the Baxs tool will help to better balance the MedSea water column C budget. It will contribute to 240 241 gain focus on the emerging picture of the C transfer efficiency (strength of the biological pump).

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243 ACKNOWLEDGEMENTS

We thank the officers and crew of *R/V* EUROPE for their assistance during work at sea. This research was supported by the French national LEFE/INSU "REPAP" project (PI. S. Jacquet). It was co-funded by the "ROBIN" project (PIs. C. Tamburini, F.A.C. Le Moigne) of Labex OT-Med (ANR-11-LABEX-0061) funded by the Investissements d'Avenir and the French Government project of the ANR, through the A*Midex project (ANR-11-IDEX-0001-02). Authors have benefited of the support of the SNO-MOOSE and SAM-MIO. BATMAN is a





- 250 contribution to the "AT POMPE BIOLOGIQUE" of the Mediterranean Institute of
- 251 Oceanography (MIO) and to the international IMBER program. The instrument (ELEMENT XR,
- 252 ThermoFisher) was supported in 2012 by European Regional Development Fund (ERDF).
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254 Figure captions

Figure 1: (a) Schematic representation of the convergence of the different estimators of oxygen 255 consumption and C remineralization rates from the "oxygen dynamics", "barium proxy" and 256 257 "prokaryotic activity" tools; (b) Location of the BATMAN cruise at the ANTARES observatory site in the NW-Mediterranean Sea (42°48'N, 6°10'E); (b) Potential temperature - salinity - depth 258 plots and isopycals for BATMAN profiles. SW: Surface Water, WIW: Winter Intermediate 259 Water, LIW: Levantine Intermediate Water, DMW: Deep Mediterranean Water. Graph 260 constructed using Ocean Data View (Schlitzer, 2002; Ocean Data View; http://www.awi-261 bremerhaven.de/GEO/ODV) 262

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Figure 2: (a) Particulate biogenic Ba_{xs} (pM) and particulate Al (nM) profiles next to the biogenic 264 Ba fraction (%) in the upper 1000 m at ANTARES. The grey area represents a biogenic Ba 265 fraction larger than 80 %. BKG: Baxs background. Baxs profile (pM) at DYFAMED : data from 266 Sternberg et al. (2008); (b) ANTARES ratio plot (green square) of integrated PHP in the upper 267 100 m over integrated PHP in the upper 500 m versus depth-weighted average (DWA) 268 269 mesopelagic Ba_{xs} (pM) over the 150- 500 depth interval. Regression of the same ratio is reported for KEOPS1 (out plateau stations) and KEOPS2 (Southern Ocean; Jacquet et al., 2015) and 270 #DY032 (PAP station, NE-Atlantic; pers. data) cruises. 271

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Figure 3: (a) Relationship between Ba_{xs} concentrations (pM) and oxygen consumption rates (µmol L⁻¹ d⁻¹) from optodes measurements (JO₂-Opt) at ANTARES; (b) Confrontation of oxygen consumption rates (mmol m⁻² d⁻¹) obtained from different methods: optodes measurements (this work), dark community respiration DCR (winkler titration; JO₂-DCR; Jacquet et al., 2015;





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396 Figure 1









399 Figure 2







400 Figure 3 401