

Dissolved rare earth elements distribution in the Solomon Sea

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 Dissolved Rare Earth Elements distribution in the Solomon Sea (Pandora, GEOTRACES cruise GP#12).

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Abstract

 Trace Elements and Isotopes (TEIs) were measured as part of the GEOTRACES PANDORA cruise (Jul-Aug 2012, R/V Atalante), among them Rare Earth Elements (REE) as pertinent tracers of land-ocean inputs and water mass transformations. This work discusses results of 21 dissolved REE (dREE) profiles measured using a trispike method in the Coral Sea and inside and at the exit of the Solomon Sea, a semi-enclosed sea with complex topography and straits. Overall, dREE –except the insoluble Ce– show nutrient like profiles, i.e. depleted at the 17 surface and enriched at depth. Illustrative Nd concentrations are ranging from \sim 5 pmol.kg⁻¹ at 18 the surface to more than 25 pmol.kg $^{-1}$ at 5000 m depth. However, dREE maxima are observed at some locations which reveal significant coastal effects, consistent with dissolved Al and Mn 20 data. These enrichments are mostly observed in the Straits (Indispensable, Solomon and 21 Vitiaz Straits) and along the island coasts. A box model allows calculating and discussing a net 22 enrichment or removal of the dissolved REE in different water layers flowing through the 23 Solomon Sea. Finally, subtle variations revealed by La, Ce, Eu anomalies and the normalized light versus heavy REE ratio (expressed as Nd/Yb) allowed the identification of specific mechanisms affecting the distribution of the different dREE. While we suspect that a coupling 26 between Ba and La could explain the significant positive La anomaly observed in our data (as 27 elsewhere in the ocean), a heavy REE as Yb seems to be correlated with the Si oceanic cycle. 28 The clear and ubiquitous positive Eu anomaly observed in the surface layers is reflecting lithogenic inputs of basaltic origin, consistent with the intensive weathering affecting the surrounding islands. These observations underline again that dREE oceanic distributions are driven by variable and complex processes, beyond those fractionating by means of an ordered response through the group as a function of atomic number.

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1 Introduction

 [1] In the southwest Pacific Ocean, the northern branch of the westward South Equatorial Current is conveyed equatorward by the low-latitude western boundary currents (LLWBCs). These currents are flowing through the semi-enclosed Solomon Sea as final pathway between the subtropical Pacific and the Equator (Fine et al., 1994; Grenier et al., 2014; Johnson and McPhaden, 1999). The LLWBCs are joining the equatorial current system, in 42 particular the eastward Equatorial Undercurrent feeding the "cold equatorial tongue" in the 43 eastern equatorial Pacific. The properties of the water masses they transport have thus the potential to impact the equatorial thermocline stratification as well as native ecosystems of the western Pacific with potential downstream effects on the eastern Pacific ones (Figure1, Germineaud et al., 2016). Hence, the Solomon Sea is a hot spot to study the water modifications when flowing from the Subtropical to the Equatorial region.

 [2] The Solomon Sea is surrounded by high and intensively weathered islands (Milliman et al 1999). Together with its complex topography and hydrography, these characteristics make this area a potential source of trace elements to the waters flowing through it. Preceding studies aimed at characterizing the chemistry of the LLWBCs upstream and downstream of the Solomon Sea (i.e: Grenier et al., 2014; Grenier et al., 2013; Slemons et al., 2010; Mackey et al., 2002; Zhang and Nozaki, 1996). However, the Solomon Sea itself was never documented so far, becoming with time a sort of "missing piece" of the geochemical map of this area.

 [3] Two exploratory oceanographic cruises were undertaken in the framework of the SPICE (Southwest Pacific Ocean Circulation and Climate Experiment) and GEOTRACES [\(www.geotraces.org\)](http://www.geotraces.org/) programs (Ganachaud et al., 2014; Ganachaud et al., 2017). The Pandora cruise (July 2012) documented a large number of hydrographic and biogeochemical parameters in the Coral and Solomon Seas while two years later the MoorSPICE cruise (March 2014) repeated the hydrographic measurements.

 [4] Dissolved chemical elements and their isotopes (so called as geochemical tracers) provide a better understanding and quantification of water mass histories and characterize the sources of key nutrient species to the oceans (Crusius et al., 1996; Elrod et al., 2004; Haley et al., 2004; Johnson et al., 2003; Nozaki, 1986). Among the "tracer world", the rare earth elements (REE) and isotopic composition of neodymium are used to quantify any lithogenic enrichment, scavenging processes and/or water mass transport when occurring in a given area (Goldstein and Hemming, 2003; Jeandel et al., 2013; Lacan and Jeandel, 2001; Tachikawa et al., 2003). Rare earth element (REE) is a group of 14 elements displaying extreme coherent characteristics from lanthanum (La) to lutetium (Lu). The light REE (LREE) refers to the lower atomic number REEs from 57 (La) to 61 (Nd); Samarium (Sm) Europium (Eu) and Gadolinium (Gd) stand for medium REE (MREE), while Dysprosium (Dy) to Lutetium are heavy REEs (HREE). Within this group, the atomic weight increases while the atomic size decreases which yields chemical fractionation processes to occur during geochemical processes by means of an ordered response through the group as a function of atomic number. In the oceanic environment, most of the previous studies concluded that not only the internal processes (i.e: Akagi, 2013; Akagi et al., 2011; De Baar et al., 1985a; Jong Hyeon

 and Byrne, 1993; Tachikawa et al., 1999) but also the external ones (i.e: Nozaki and Alibo, 2003a; Nozaki and Alibo, 2003b; Sholkovitz et al., 1994; Rousseau et al., 2015; Wang and Yamada., 2007) could fractionate the REE distribution. The internal processes occurring all along the water column can be resumed as dissolved-particulate exchanges which result from biological uptake-remineralization and/or adsorption-desorption onto reactive particle 83 coatings and/or (co)precipitation-dissolution. In addition, dREE could be released to the open ocean from river discharge, atmospheric dust, hydrothermal plume or exchange at the land- ocean interface, considered as external inputs. Understanding the fate of these important 86 tracers in the modern ocean is therefore a key issue.

 [5] This work characterizes the dREE concentrations along the whole water column at 21 stations collected between the entrance of the Coral Sea and the exiting straits of the 89 Solomon Sea. The geochemical data are coupled with the associated hydrological parameters and the water mass transports, providing an essential view on water mass pathways. This strategy allows us to describe and quantify the modification of geochemical parameters during south-north transit of the waters through the Solomon Sea. Our results are also compared with other geochemical parameters (e.g: Al, Mn) which are concurring to validate the enrichment of lithogenic origin observed in the Solomon Sea. Relationships between dREE, dissolved Ba and nutrient data are also discussed in order to reveal the influence of the biological activity REE fractionation.

 [6] Section 2 describes the sampling procedure, sample preservation and analytical protocol while section 3 presents the hydrological context. Section 4 presents the resulting dREE profiles and their PAAS-normalized patterns. Section 5 is the discussion: it presents a simple box model to estimate the dREE Solomon Sea budgets in different density layers, the enrichment of the waters along their pathways, and provides a discussion around the fractionation observed in the REE patterns (La, Ce, Eu anomalies), the presumed associated mechanisms and the control of the HREE fate by the dissolved silica.

2 Material and Methods

2.1. Sample collection

 $\frac{43}{44}$ 107 45 108 $\frac{46}{17}$ 109 48 110 $\frac{49}{20}$ 111 51 112 52 113 $\frac{53}{54}$ 114 55 115 116 [7] 143 seawater samples were collected at 21 stations during the PANDORA cruise (July- August 2012, onboard R/V *Atalante*). The sampling locations are reported in Figure 1b. Nine stations (stations 04, 10, 13, 20, 21, 29, 34, 36 and 82) were located in the Coral Sea and at the southern entrance of the Solomon Sea in order to characterize the water masses entering the Solomon Sea. Stations 04 and 10 were sampled to characterize the North Vanuatu Jet (NVJ) and North Caledonia Jet (NCJ), respectively. Stations 13, 20 and 21 were collected before and after the Indispensable Strait in order to identify any modification of the waters when flowing through this strait. Stations 29, 34 and 36 tried to catch the complex hydrological features at the entrance of the Solomon Sea (Cravatte et al., 2011; Davis et al., 2012; Germineaud et al., 2016). The remaining 12 stations are located in the "body" of the Solomon Sea as well as in the 3 straits through which waters are flowing out (i.e: Vitiaz Strait, St George's Channel and Solomon Strait).

 $\frac{2}{3}$ 120 4 121 $\frac{9}{0}$ 125 11 126 118 \qquad [8] Salinity (S), potential temperature (θ) and dissolved oxygen (dO₂) were measured on 119 board using sensors mounted at the base of the rosette. Salinity and oxygen sensors were calibrated and adjusted after the cruise using the chemical measurements of these parameters on discrete samples (Ganachaud et al., 2017). Shipboard and Lowered Acoustic 122 Doppler Current Profiler (ADCP) data and other samples for various chemical analyses were 123 also acquired during the cruise for the seawater characterization in trace metals, nutrients 124 and other biological and chemical parameters. The online cruise report [\(http://www.obs](http://www.obs-vlfr.fr/proof/php/pandora/xdat%20alist1.php?xxop=pandora&xxcamp=pandora)[vlfr.fr/proof/php/pandora/xdat alist1.php?xxop=pandora&xxcamp=pandora\)](http://www.obs-vlfr.fr/proof/php/pandora/xdat%20alist1.php?xxop=pandora&xxcamp=pandora) and the synthesis article of Ganachaud et al. (2017) provide more details on the numerous operations 127 conducted in the framework of PANDORA.

128 [9] Seawater samples dedicated to dREE analysis were collected using 22 12 L Niskin bottles mounted on a rosette. Aliquots of 500 mL were rapidly filtered through 0.4 µM pore size, 47 mm diameter SUPOR membranes in the R/V Atalante humid laboratory. Filtered water was transferred into pre-cleaned low density polyethylene (LDPE) bottles and immediately acidified to pH≤2 by addition of suprapur HCl 30%. All consumable material was 133 acid-cleaned before the cruise. Note that samples from station 82 and some duplicates from station 73 and 77 were not filtered. Replicate samples were also taken at some stations in 135 order to validate the data, identify particle/dissolved interaction and control the blank of the filtration system (e.g. at station 73).

2.2. Analytical procedure

 $\frac{30}{31}$ 139 32 140 34 141
35 142 36 143 $\frac{37}{38}$ 144 $\frac{41}{42}$ $\frac{140}{147}$ 43 148 $\frac{44}{45}$ 149 46 150 $\frac{47}{10}$ 151 $\frac{48}{49}$ 152 50 $\frac{51}{52}$ 154 53 155 138 [10] dREE concentrations were determined using the LEGOS protocol (Lacan and Jeandel, 2001; Tachikawa et al., 1999). Briefly, dREE were extracted from the seawater aliquot by a co-precipitation with iron hydroxides, followed by purification through ion-exchange column 141 and measured with a High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS). In details, a trispike solution containing 150 Nd (97.84%), 153 Eu (97.84%), and 174 Yb 143 (94.9%) was added to the acidified seawater aliquots of 250 mL or 500 mL. Approximately 2.5 mg of purified FeCl₃ diluted in 0.1M HCl was then added to the samples. The homogenization 145 was ensured by a continuous shaking of the sample during 24h and a subsequent 24h resting 146 state before performing the co-precipitation. Then, the pH was increased to 8±0.5 by adding 147 suprapur NH₄OH yielding the iron hydroxides to co-precipitate the dREE. The dREE-Fe precipitate was then rinsed and separated from the seawater by successive centrifugations. This rinsing step was repeated between 5 to 7 times and the precipitate was later dissolved in 1 mL of 6M HCl and then loaded on an anion exchange column packed with 2 mL of AG1-X8 resin, in order to purify the dREE fraction from Fe. dREEs were then eluted from the column using 4 mL of 6M HCl and evaporated to dryness. Finally, the residue was dissolved again with 5 mL HNO₃ 0.32M spiked with an internal standard (In-Re, 100 ppt), which is the appropriate solution to measure the concentrations on a sector field Inductively Coupled Plasma Mass Spectrometer (THERMO ELEMENT XR™ ICP-MS).

 $\frac{54}{55}$ 156 56 157 $\frac{58}{59}$ 159 [11] Recoveries of the whole experiment (including sensitivity variations during the ICPMS sequence) were precisely determined by comparing the Nd, Eu and Yb concentrations 158 calculated by Isotopic Dilution (ID-CONC) with that measured by external calibration (EXT-CONC). The ratio (EXT-CONC)/(ID-CONC) for these 3 elements were then linearly

 $\frac{2}{3}$ 162 3 $4\quad 163$ $\frac{9}{0}$ 167 10 11 168 160 (interpolated and extrapolated to be applied to the remaining dREE concentrations, 161 measured by external calibration only. On the average, recoveries of more than 80% were obtained for the light REE, and around 77% for the middle and heavy REE. Our method based on 2 or 3 spikes followed by an (inter/extra)polation was validated by comparing results 164 obtained using 10 spikes on the same seawater samples, either in the framework of T. 165 Rousseau thesis (Rousseau et al., 2013) or in the recent work of M. Behrens (Behrens et al., 166 2016). During the ICP-MS analysis, the use of a desolvating nebulizer system (ARIDUS II) considerably minimized the oxide interference formation (Chung et al., 2009; Grenier et al., 2013; Pahnke et al., 2012). This is notably effective for the barium oxide formation reduction, 169 which subsequently improves the analytical accuracy for 151 Eu and 153 Eu.

 $\frac{15}{16}$ 171 17 172 $\frac{18}{10}$ 173 $\frac{19}{20}$ 174 $\frac{22}{23}$ 176 170 [12] Replicate measurements were conducted on filtered (4 replicates, station 73, 1650 m) and non-filtered samples (3 replicates at 1650 m of station 73 and 4 replicates at 1200 m of station 82). Filtered light REE (dLREE) concentrations agree within 8% for La, 14% for Ce and 4% for Pr and Nd; filtered middle (dMREE) and heavy (dHREE) concentrations agree within 8% for Sm, 11% for Eu and less than 4% for the remaining REE. Non-filtered 175 concentrations are agreeing within less than 4% for all the LREE (including Ce) and 7% for MREE and HREE.

 $\frac{24}{177}$ $\frac{25}{26}$ 178 27 179 $\frac{28}{39}$ 180 30 181 $\frac{32}{33}$ 183 34 184 [13] The average chemical blank values were established on 20 measurements. Blank levels represent less than 2% of the LREE signals and less than 0.7% for MREE and HREE ones. Due to the very low Ce concentration in our samples, the dCe blanks represent 14±9% of the sample signal. In addition, the blank of our on-board filtration system was checked by filtering twice the same samples. No noticeable variation of concentration was observed, assessing 182 the cleanliness of our systems. Finally, our full dREE analytical procedure was validated by our successful participation to two GEOTRACES intercalibration exercises (Behrens et al., 2016; van de Flierdt et al., 2012).

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36 **185** 36 37 186 $\frac{38}{39}$ 187 39 40 $\frac{41}{42}$ 189 $\frac{42}{43}$ 190 43 44 191 $\frac{45}{46}$ 192 46 47 193 $^{48}_{10}$ 194 $\frac{49}{50}$ $\frac{154}{195}$ 50 51 $\frac{52}{53}$ 197 53 54 198 $\frac{55}{26}$ 199 $\frac{156}{57}$ 200 57 58 201 59 [14] Together with REE analysis, the dissolved Ba were also measured follow this protocol: fifteen mL of unfiltered seawater were collected in pre-cleaned polypropylene bottles (rinsed three times with the same seawater sample), acidified with 15 μ L of HCl (10 M, Optima 188 grade) and kept at room temperature for later analysis. Dissolved Ba concentrations were 189 measured using an isotope dilution (ID) method (Freydier et al., 1995; Klinkhammer and 190 Chan, 1990) by high resolution -inductively coupled plasma- mass spectrometry (HR-ICP-MS). This method was adapted to a Thermo Finnigan Element XR instrument (MIO, Marseille). The dissolved Ba measurements presented here are the sum of dissolved Ba and a very small fraction (generally <1 % of total Ba) that is generated from the particulate Ba pool as a result of the acidification. For the sake of simplicity, we use the term of dissolved Ba. Samples (0.5 mL) were spiked with 300 µL of a 135Ba-enriched solution (93 % 135Ba; 95 nmol.kg⁻¹) and diluted with 15 mL of acidified (2 % HNO3, 14 M, Optima grade) Milli-Q grade water (Millipore). The amounts of sample, spike and dilution water were assessed by weighing. Reproducibility of this method is 1.5 % (1 RSD) as tested on repeated preparations of the reference solution SLRS-5 (NRC-CNRC river water reference material for trace metals; 101.9 ± 3.6 nmol kg^{-1}). The limit of detection, calculated as three times the standard deviation of the procedural blank, is 0.09 nmol.kg $^{-1}$.

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203 3 Hydrological context

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4 \quad 205\n\end{array}$ 5206 $\frac{6}{7}$ 207 8 208 $\frac{10}{11}$ 210 12 211 $\frac{13}{14}$ 212 15 213 $\frac{16}{15}$ 214 $\frac{17}{18}$ 215 204 [15] Coral and Solomon sea hydrological properties have been the subject of serveral surveys since the 60s. Water mass properties were discussed in miscellaneous works since 206 then (e.g. Tsuchiya, 1981; Tsuchiya et al., 1989; Qu and Lindstrom, 2002; Grenier et al., 2013; Kessler and Cravatte, 2013; Ganachaud et al., 2014). Recently, Germineaud et al. (2016) 208 presented a detailed description of the currents and water masses in the Solomon Sea based 209 on the PANDORA (2012) and MoorSPICE (2014) cruise data. The description proposed here is mostly based on this last work together with the thorough description of the Southwest Pacific currents conducted by Grenier et al. (2011; 2013, 2014). The water mass nomenclatures are varying among authors; the names used in this study are following those 213 proposed by Grenier et al. (2013), Tomczak and Godfrey (2003), and Tomczak and Hao (1989) in order to avoid any confusion when describing the water masses, especially in the layers characterizing the thermocline.

 $\frac{19}{20}$ 216 20 21 217 22 $\frac{23}{24}$ 219 24 25 220 [16] The general circulation scheme, current names and sampling details of the different stations used in this study are given in Figure 1. Figure 2 proposes a compilation of the 218 property plots observed at the different stations, together with the identification of the main water masses sampled during the cruise. The last column of Table 1 also recalls the water masses corresponding to the collected seawater samples.

 $\frac{26}{27}$ 221 27 28 $\frac{29}{30}$ 223 30 31 224 $\frac{32}{22}$ 225 $\frac{33}{34}$ 226 34 35 [17] Water properties in the Southwest Pacific can be traced from the Coral Sea to the 222 Solomon Sea, in part through the Low Latitude Western Boundary Currents (LLWBCs) flowing toward the Equator (Figure 1). The LLWBCs are initially fed by the westward South Equatorial Current (SEC) (Qu and Lindstrom, 2002; Tsuchiya et al., 1989), dividing into several zonal currents when encountering islands in the Coral Sea. These zonal currents, some of them extending deep, transport several water masses that we choose to present here following 227 increasing density.

- $\frac{37}{38}$ 228 3.1. Thermocline Waters
	- 229 *3.1.1.Upper thermocline: Tropical and Equatorial Waters*

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 45 232 [18] In the Coral and Solomon Seas, the salty South Pacific Tropical Waters (SPTW) are 231 flowing in the upper thermocline (\sim σ θ = 24.3-25.3 kg.m-3). This tropical water can be divided in two main branches.

46 47 233 $\frac{48}{10}$ 234 49 235
50 235 50 51 236 $\frac{52}{53}$ 237 53 54 238 $\frac{55}{2}$ 239 $\frac{56}{57}$ 240 58 241 $\frac{59}{60}$ 242 [19] The northern branch of the SPTW is called the South Pacific Equatorial Water (SPEW) and enters the Coral Sea north of the Vanuatu Archipelago, transported by the North 235 Vanuatu Jet (NVJ) (Kessler and Cravatte, 2013; Tomczak and Godfrey, 2003; Tomczak and Hao, 1989; Tsuchiya et al., 1989). The SPEW originates from the subtropical central South Pacific (~20oS, 110°W), subductes in the high surface evaporation zone (HSEA), characterized by a maximum in sea surface salinity (see Figure 1 of Grenier et al., 2013). The SPEW is thus marked by a maximum in salinity (~S=36.0) at $\sim \sigma_\theta$ =24.5 kg.m⁻³ (Kessler, 1999; Qu and Lindstrom, 2002) and relative high oxygen (~135 μ mol.kg⁻¹; Grenier et al., 2013). After entering in the Coral Sea, the SPEW follows two pathways to reach the Solomon Sea: the first 242 one is directly entering by the southern entrance of the Solomon Sea while the second is

 $\frac{2}{3}$ 245 243 conveyed by the Gulf of Papua Current (GPC) before entering the Solomon Sea at its 244 southwestern end (see Figure 3 and Figure 5 of Cravatte et al., 2011; Ganachaud et al., 2014). During Pandora, SPEW was well identified at station 10 (Figure 2).

5 246 $\frac{7}{8}$ 248 9 249 12 251 15 253 16 254 [20] The southern branch of the SPTW enters the Coral Sea mainly south of the Vanuatu 247 Archipelago, conveyed by the North Caledonian Jet (NCJ) (Ganachaud et al., 2014; Gasparin et al., 2011; Germineaud et al., 2016; Grenier et al., 2013). This tropical water is then transported westward to the Australian coast where it bifurcates equatorward and poleward. 250 The equatorward branch is carried by the GPC, and enters the Solomon Sea where it mixes with the SPEW described above to form the New Guinea Coastal Undercurrent (NGCU) 252 flowing equatorward (Cravatte et al., 2011). At the entrance of the Coral Sea, this water mass 253 is slightly denser (~ σ_{θ} =24.8 kg.m⁻³), less saline (S~35.6) and richer in oxygen (~165 µmol.kg⁻¹) than those of the northern branch (see station 4, Figure 2).

 $\frac{19}{20}$ 256 $\frac{22}{22}$ 258 24 259 $\frac{26}{27}$ 261 28 262 $\frac{29}{30}$ 263 31 264 32 265 255 [21] Inside the Solomon Sea, the NGCU splits south of Woodlark Island and then remerges at its northern side, to finally bifurcate again into two branches south of New Britain Island. 257 The first branch flows westward towards the Bismarck Sea through the Vitiaz Strait while the second one is conveyed eastward by the New Britain Coastal Undercurrent. It exits the 259 Solomon Sea northward by the St George's Undercurrent (SGU) and the New Ireland Coastal 260 Undercurrent (NICU) through St George's Channel and Solomon Strait, respectively (Cravatte 261 et al., 2011; Ganachaud et al., 2014; Ganachaud et al., 2017; Germineaud et al., 2016). Since the SPTW in the Solomon Sea results from the mixing between two water masses of minor differences which are referred above, its characteristics are fairly high oxygen content (140-145 μ mol.kg⁻¹), and high salinity (~S=35.7, see station 34, 36, 42, 43, 57, 60, 71, 73 and 77 in figure 2).

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266 *3.1.2. Lower thermocline: Central Water and Mode Water*

 $\frac{36}{27}$ 267 38 268 $\frac{39}{12}$ 269 $\frac{40}{41}$ 270 42 271 $\frac{43}{11}$ 272 44 45 273 46 274 $\frac{47}{48}$ 275 49 276 $\frac{50}{51}$ 277 52 278 53 279 [22] Lying just underneath the upper thermocline water and considered as the lower 268 thermocline water, the Western South Pacific Central Water (WSPCW) is identified in our 269 research area, displaying thermostad characteristics (Grenier et al., 2014; Qu et al., 2008; Tsuchiya, 1981) and a very loose stratification at about 300 m depth. WSPCW is described by potential density centered at 26.4 kg.m-3 and high salinity due to its origin, north of New Zealand (Tomczak and Hao, 1989). High oxygen content WSPCW (mean $O_2=160 \text{ kg.m}^{-3}$) is conveyed into the Coral Sea in its southern part, through the deep NCJ (Sokolov and Rintoul, 2000; Tomczak and Godfrey, 2003; Tsuchiya et al., 1989). During its transportation through the Coral Sea, the Gulf of Papua and inside the Solomon Sea (Kessler and Cravatte, 2013), this water mass loses its oxygen as a result of mixing. Near the straits, it mixes with older, deoxygenated water originating from the southeastern Pacific Ocean and entering the Solomon Sea through Solomon Strait. A drop of dissolved oxygen values from \sim 160 kg.m⁻³ at the southern entrance of the Solomon Sea to \sim 130 kg.m⁻³ in its northeastern part is observed.

55 280 $\frac{57}{58}$ 282 59 283 [23] Below the WSPCW, another mode water, with no salinity or oxygen extremum, is 281 identified. It is named the Subantarctic Mode Water SAMW (σ_{θ} = 26.5-27 kg.m⁻³) and enters the Coral and Solomon Seas from the south, (Grenier et al., 2013; McCartney, 1977). It originates from the southeastern Southern Ocean by subduction north of the Antarctic

 $\frac{2}{3}$ 286 4 287 284 Circumpolar Current (Hanawa, 2001). This water mass is centered on $\sim \sigma_\theta = 27$ kg.m⁻³ and is 285 characterized by a low salinity (~34.5) and high oxygen content (~175 kg.m⁻³) because of its origin (Qu et al., 2009). In the Coral and Solomon Seas, SAMW keeps its original characteristics and contributes to the formation of 13° C Water (Qu et al., 2009).

288 3.2. Intermediate Waters

 $\frac{10}{11}$ 291 289 \qquad [24] The Antarctic Intermediate Water (AAIW; σ^{θ} ~27.2kg.m⁻³) is identified in the southern 290 part of the studied region by a salinity minimum (~S=34.3-34.5) and an oxygen maximum (\sim O₂=200-300 µmol.kg⁻¹, Qu and Lindstrom, 2004). The AAIW circulation in the South Pacific 292 follows the wind-driven subtropical gyre circulation and flows equatorward through the Coral Sea. It enters the Solomon Sea through the LLWBCs (Bostock et al., 2010; Germineaud et al., 2016; Qu and Lindstrom, 2004; Tomczak and Godfrey, 2003). From the Coral Sea to the 295 equator, the AAIW becomes slightly denser and less oxygenated (~ σ_{θ} =27.26 kg.m⁻³; O₂=160-190 μ mol.kg⁻¹) due to remineralization of organic material setling from the surface and 297 diapycnal mixing with lower oxygenated waters.

 $\frac{20}{21}$ 298 $\frac{23}{24}$ 300 25 301 $\frac{26}{9}$ 302 $\frac{27}{28}$ 303 $\frac{30}{31}$ 305 [25] Another intermediate water identified in our study area is the Equatorial Pacific 299 Intermediate Water (EqPIW ; $\sim \sigma_\theta = 27.3$ kg.m⁻³), which is originally formed from a combination of AAIW and upwelled Pacific Deep Water (Bostock et al., 2010). In our study, it is suggested that part of this water mass enters the Solomon Sea from the north-east through Solomon Strait (Germineaud et al., 2016) and mixes then with AAIW as proposed in Figure 1 of Bostock et al. (2010). The distinct characteristics of this water mass is a salinity higher than that of 304 AAIW (~S=34.5-34.6) and a significantly lower oxygen concentration (~O₂=75-125 µmol.kg⁻¹). It is found at a density of 27 kg.m⁻³ at station 43 and 46. Moreover, the oxygen plot of station 306 43 show that EqpIW and AAIW are interleaving near 700 m depth.

3.3. Deep and Bottom Waters

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36 308 $\frac{37}{22}$ 309 $\frac{38}{39}$ 310 40 311 $\frac{41}{42}$ 312 42 313
43 313 [26] The deep and bottom waters within the Coral and Solomon Seas have been poorly documented since the first observations summarized in Reid (1986, 1997) and their pathways and fates are not clearly understood. They are strongly constrained by the topography (Johnson and Toole, 1993; Kawabe and Fujio, 2010; Roemmich et al., 1996; Tsimplis et al., 312 1998). Their pathways, origins and properties are described in Germineaud et al. (in preparation).

 44 ₄₅ 314 46 315 $\frac{47}{40}$ 316 $\begin{array}{@{}c@{\hspace{1em}}c@{\hspace{$ 50 $\frac{51}{52}$ 319 53 320 $\frac{54}{55}$ 321 [27] The Upper Circumpolar Deep Water (UCDW) is observed between 1000 m and 3500 m in the studied area. This water mass has been depleted in oxygen since its origin in the Antarctic Circumpolar Current (ACC) (Reid, 1986; Talley, 2007; Wijffels et al., 2001). In this study, UCDW is characterized by relatively high salinity and low oxygen content with a 318 pronounced minimum (~S=34.6, ~O₂=140 µmol.kg⁻¹) at ~ σ_{θ} =27.65 kg.m⁻³ at almost all of our stations (Figure 2). Germineaud et al. (2016) suggests that the UCDW can be divided into two sublayers which are the upper extent and lower extent UCDW, with potential density anomaly (σ_{θ}) ranges of ~27.4-27.65 and 27.65-27.76, respectively.

56 $\frac{57}{58}$ 323 $\frac{58}{59}$ 324 59 60 [28] Just beneath the UCDW, the Lower Circumpolar Deep Water (LCDW; Kawabe and Fujio, 2010; Reid, 1997; Tsimplis et al., 1998) is identified by a salinity maximum reaching 324 34.72–34.73 and a decrease of its silicate content when compared to the UCDW (Orsi et al.,

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 $\frac{2}{3}$ 327 4 328 7 330 325 1999). The LCDW transport is supposed to be limited from the Tasman Sea to the Coral and 326 Solomon Seas because this last one is so far considered as a sealed area below 3500 m, separated from the outer world by islands and sills (Germineaud, 2016; Sokolov and Rintoul, 328 2000). Curiously, we clearly identified the LCDW imprint in our profiles, and an unexpected 329 oxygen concentration increase with depth, which underlines that the topography, and the possible pathways and fate of this water mass are still unclear (Germineaud et al., in 331 preparation).

4 Results

4.1. Dissolved REE concentrations

[29] The dissolved concentrations measured for the 14 REEs at the different stations are compiled in Table 2.For simplicity, only the vertical distributions of dissolved Lanthanum (dLa), Neodymium (dNd), Europium (dEu) and Ytterbium (dYb) are shown in Figure 3. dLa and dNd represent the dissolved LREE while dEu and dYb represent the dMREE and dHREE, respectively.

22 339 $\frac{24}{25}$ 341 26 342 $\frac{27}{28}$ 343 29 344 $30\quad 345$ [30] The dREE concentrations display low values at the surface and increase with depth, 340 showing a vertical profile shape similar to that of nutrients although not completely depleted in the surface waters (Figure 3). The dLa concentrations are increasing from \sim 4 pmol.kg⁻¹ in the surface water to ~15 pmol.kg⁻¹ at ~1000 m; dNd profiles are varying from ~5 pmol.kg⁻¹ in the euphotic zone to ~10 pmol.kg⁻¹ at intermediate layer followed by an ~2.5-fold increase towards the bottom. Typical dEu and dYb profiles show the same kind of gradients as dLa and dNd but with lower concentrations $\left($ <1 pmol.kg⁻¹ for dEu and <10 pmol.kg⁻¹ for dYb).

32 346 $\frac{33}{24}$ 347 34 34
35 348 36 349 $\frac{37}{38}$ 350 39 351 $\frac{40}{11}$ 352 41 352
 42 353 [31] The surface depletion and enrichment at depth are consistent with the surfacescavenging and depth-dissolution hypothesis characterizing the fate of these trivalent 348 elements onto particulate carrier phases (oxides, hydroxides, organic matter) along the water column (De Baar et al., 1985a; Elderfield, 1988; Garcia-Solsona et al., 2014; Sholkovitz et al., 1994; Takebe, 2005). The concentration ratio between the deepest samples (deeper than 3000 m) and shallowest samples is larger than 4, indicating a significant release of the REE from the particles in the deepest layers. Beyond the observed general concentration increase, the vertical shape of the profiles show subtle but interesting variations:

- Down to 3000 m, all the concentrations linearly increase, although the dYb profile is always slightly more convex than the 3 other dREE ones.
- In the southern part of our study (Coral Sea and Solomon Sea entrance, Figure 3a), a break is observed in the linearity at 3000 m, with dREE concentration values slightly lower between 3000 and 4000 m.
- Station 60 profiles, in the northern part of the Solomon Sea, show a local maximum between 4000 and 5000 m, dREE concentrations being maximal in this layer and then decreasing toward the bottom. The convex shape of dYb is the most pronounced at this station (Figure 3c).
- 363 On the average, dREE concentrations are slightly enriched within the Solomon Sea compared with the sites located outside of it. For example, dNd average value is of ~3.5 pmol.kg⁻¹ in the Solomon Sea for the isopycnal layer 24 kg.m⁻³ < σ _e < 26 kg.m⁻³

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366 while of 2.5 pmol.kg⁻¹ for the same density layer in the Coral Sea and in the east of 367 the Solomon archipelago (see station 04, 10, 34 and 71, Figure 3).

> • Figure 3e shows a slight maximum at station 21, suggesting an input of Solomon Archipelago material into seawater passing through Indispensable strait

[32] In addition to these features affecting the profiles, local enrichments are observed at 371 specific stations and depths as at the surface of stations 36, 57 and 77, very likely reflecting 372 the proximity between these stations and the coast. Within the thermocline some layers show enriched dREE concentrations [e.g: around 500 m at station 42, 46, 57, 77, in the 374 intermediate waters (~700 m) at station 13, 21, 34 and at 980 m at station 29].

13 375 $\frac{15}{16}$ 377 17 378 $\frac{18}{10}$ 379 20 380 $\frac{22}{23}$ 382 24 383 $\frac{25}{25}$ 384 $\frac{26}{27}$ 385 [33] Dissolved cerium (dCe) concentrations are reported in Table 1 and some data will be 376 shown later as part of the discussion. As often observed in seawater where the oxidized Ce(IV) is poorly soluble and then behaves differently to the remaining trivalent REEs, dCe shows a reverse behavior compared to the other dREEs, with high concentrations at the top of the water column, which decreasing at intermediate levels before increasing again in the deep and bottom waters due to its preference for scavenging (see station 29, 42, 71 and 73, 381 Table 1) (De Baar et al., 1983; De Baar et al., 1985a; Elderfield, 1988; Goldberg et al., 1963; Liu et al., 1988; Piepgras and Jacobsen, 1992; Sholkovitz et al., 1994; Tachikawa et al., 1999). 383 However, consistently with the other dREEs, dCe maxima are observed at some specific locations: surface layers at station 36 and 77, close to the surface and at 735 m at station 34 and slightly deeper (934 m) at station 29 (Table 1).

4.2. Comparison with previous studies

 $\frac{30}{31}$ 387 32 388 $\frac{33}{36}$ 389 34 ³⁰⁹
35 **390** 36 391 $\frac{37}{38}$ 392 39 393 $\frac{40}{11}$ 394 42 395 [34] Two previous studies analyzed samples at the entrance of the Solomon Sea and in the Coral Sea (Grenier et al., 2013; Zhang and Nozaki, 1996), allowing us to compare our data with published values. Figure 4 shows the locations of these stations and the dissolved REE concentrations as a function of potential density in order to compare the dREE values in the same isopycnal layers. This figure also highlights the excellent agreement between our data and these previous results. The minor difference observed between the surface dLa concentrations at SA-7 and at station 82 of our study likely reflects the dissimilarity in our sampling locations and times of the year, in this region of high eddy variability (Keppler et al., 2018).

 $\frac{43}{44}$ 396 45 397 $\frac{47}{48}$ 399 49 400 $\frac{50}{51}$ 401 52 402 53
54 **403** [35] In Vitiaz strait, a striking similarity between our results (station 077) and Grenier et al. (2013) one (EUC-30) is also observed, despite the difference in sampling times (Figure 4) in 398 this highly variable and turbulent region. Station 077 is located in Vitiaz strait which is narrow and relatively shallow (1200 m deep) in comparison with Solomon Sea average depth. The 400 continental influence is therefore suggested to be high and dominant over the influence on dissolve concentration of internal oceanic processes variability. This suggests that the REEs concentrations are "buffered" by interplay of different processes.

4.3. Dissolved REE patterns

56 404 57 405 $\frac{58}{50}$ 406 60 407 [36] Fractionation of the dREE from each other while submitted to oceanic processes (uptake, remineralization, freshly weathered from the continent or not...) could be identified using the normalization of dREE concentrations in seawater to those contained in shale, a 407 material representing the average crustal geochemical composition. Here we used the Post408 Archean Australian Shale or "PAAS" (McLennan, 1989). The PAAS-normalized REE patterns 409 are presented in Figure 5.

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6 412 $\begin{smallmatrix} 8\\ \ \, 0\\ \ \, 414 \end{smallmatrix}$ 10 415 13 417 [37] The main characteristics of the dREE patterns observed in the Coral and Solomon Seas 411 are consistent with those found in the literature: the obvious negative dCe anomalies reflect the impact of the poor solubility and preferential scavenging of this element. The (dNd_n/dYb_n) 413 ratio, which gives information about the dLREE versus dHREE slope evolution, is maximum in surface, decreasing from \sim 0.3 to approximately 0.1 at intermediate level (\sim 1000 m), from where it increases again in the deep and bottom waters. These observations agree with 416 previously published results (Bertram and Elderfield, 1993; De Baar et al., 1985a; Tachikawa et al., 1999; Garcia-Solsona et al., 2014; Grenier et al., submitted; Grenier et al., 2013; Zhang 418 and Nozaki, 1996).

16 419 $\frac{18}{19}$ 421 $\frac{21}{22}$ 423 [38] dREE patterns are relatively flat in surface waters, which seems to indicate that recent 420 lithogenic inputs are affecting these upper layers. The evolution of the pattern shape with depth reflects the differential scavenging along the water column. A slight local maximum is 422 often observed for the dMREE, as already noticed by Grenier (Grenier et al., 2013) in the same area.

24 424 5 Discussion

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5.1. Nd and dREE enrichments within the Solomon Sea

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 28 426 28 29 427 $\frac{30}{31}$ 428 31 32 429 $\frac{33}{34}$ 430 34 430
 35 431 35 36 432 $\frac{37}{38}$ 433 38 39 434 40 $\frac{41}{42}$ 436 42 [39] A simple box model was built for the Solomon Sea, allowing us to estimate the dREE budget for different isopycnal layers between its southern entrance (southern section) and its northern exits (Vitiaz Strait, St George's Channel and Solomon Strait). The box model proposed here aims at identifying whether dREE (but more specifically dNd) concentrations get enriched, depleted, or stay constant while crossing the Solomon Sea and determining the related input (or output) net fluxes. This is a preliminary step to further developments that will include the on-going measurements of Nd isotopic compositions, allowing us a better 433 quantification of exchange processes, if any. The scheme of the box model is proposed in Figure 6. This box model is applied to the upper thermocline layer (sigma 24-25.3 kg.m⁻³), the 435 lower thermocline layer (sigma 25.3-26.9 kg.m⁻³), the intermediate waters (sigma 26.9-27.4 436 kg.m⁻³), and the deeper UCWD waters (sigma 27.4-27.65 and 27.65-27.76 kg.m⁻³).

 $\frac{43}{44}$ 437 44 45 438 46 47 49
 48 440 48 49 441 $\frac{50}{51}$ 442 51 52 443 53 $\frac{54}{55}$ 445 55 56 446 $\frac{57}{58}$ 447 58 59 448 [40] Owing to the complexity of the Solomon Sea currents (see section 3), we hypothesized a slightly simplified circulation scheme. Our box model considers the Solomon 439 Sea as a closed area at steady state and assumes that incoming and exiting water fluxes are balanced (Figure 6a). Two upstream sources (incoming NGCU and direct NVJ) are feeding the Solomon Sea across the southern entrance and three downstream fluxes (SGU, NICU and NGCU) are exiting from it through the different straits (NGCU through Vitiaz Strait, SGU 443 through St George's Channel, NICU through Solomon Strait). The required parameters to 444 achieve the model calculation are the water mass transports and the Nd concentrations of each layer. Water flowing equatorward into the Solomon Sea includes the transports of the NGCU (W_F), and of the direct inflow (W_N). Meanwhile, water leaving the Solomon Sea gathers the fluxes exiting at the Solomon Strait (W_S), the St. George's Strait (W_G) and Vitiaz Strait (W_V). Respective dissolved Nd concentrations considered here are Nd_E, Nd_N at the southern

449 entrance and Nd_S, Nd_G and Nd_V at the northern exits (Figure 6a and b). Under the hypothesis 450 that diapycnal mixing is weak in this area, we obtain in each density layer the equation:

$$
W_{E} \cdot [Nd]_{E} + W_{N} \cdot [Nd]_{N} + F_{tot \, PANDORA} = W_{S} \cdot [Nd]_{S} + W_{G} \cdot [Nd]_{G} + W_{V} \cdot [Nd]_{V}
$$
 (1)

Where:

F_{tot PANDORA} is the total net flux into seawater from the surrounding coasts.

453 [41] The transports are computed in each density layer using the PANDORA cruise data 454 (Ganachaud et al., 2016; Germineaud et al., 2016; Germineaud et al., in prep). Currents were 455 recorded along the ship track with Shipboard Acoustic Doppler Current Profilers (S-ADCPs) with a vertical extent of around 1000-1300 m. S-ADCPs were rotated to estimate the current perpendicular to each of the box model section (Germineaud et al., 2016). At depths below 1000 m, they are combined with geostrophic velocities estimated with CTD station pairs, and referenced to 3000 m depth, or to the deepest common level of the station pairs.

23 461 $^{24}_{27}$ 462 $\frac{25}{26}$ 463 27 464 $\frac{28}{39}$ 465 [42] Transports computed across the southern entrance do not balance the summed transports at the exits, as they were estimated during instantaneous transects. For the purpose of this study, relying on a steady state hypothesis, velocities are adjusted with an inverse model to allow the mass, salt and heat conservation (Germineaud et al., 2016; 464 Germineaud et al., in prep). All water transports in distinct layers associated with their uncertainties are given in Table 4.

 $\frac{30}{21}$ 466 $\frac{31}{32}$ 467 33 468 $\frac{34}{35}$ 469 36 470 $\frac{37}{12}$ 471 $\begin{array}{@{}c@{\hspace{1em}}c@{\hspace{$ 40 473 [43] The calculation is reported in Figure 6c for Nd in the lower thermocline layer, and 467 budgets of the other layers are reported in Table 4. The only missing dREE concentration data was for the upper thermocline at station 29. We therefore estimated these values using its 469 neighbor stations due to their similarity in dREE concentrations (stations 04, 34 and 36). The sign of F_{tot} $_{\text{PANDORA}}$ indicates whether external input (when positive) or subtraction by scavenging process (when negative) is dominating the Nd fate along the pathway of the different water layers. A Monte Carlo statistic method was used to estimate uncertainties of the fluxes.

42 474 43 475 $\frac{44}{15}$ 476 46 477 $\frac{47}{40}$ 478 49 479 50 $\frac{51}{52}$ 481 53 482 $\frac{54}{1}$ 483 55 [44] A significant positive net flux (F_{total PANDORA} = 145.1 ± 45.8 t(Nd).yr⁻¹; Figure 6c) is observed in the Lower Thermocline Layer, suggesting that waters transported equatorward through the Solomon Sea are enriched in dNd. This is consistent with Grenier et al. (2014) who found enrichment in the lower thermocline layer downstream the Solomon Sea and suggested that this enrichment occurred inside the sea itself. Enrichments are also observed in the other layers, except for IW. However, the large uncertainties affecting the calculated fluxes prevent us to draw firm conclusions for these layers (Table 4). Our flux estimations are approximately 50 times those of Grenier et al. (2014). This difference likely reflects that the whole region is considered here whereas Grenier et al. (2014) only focused on inputs into specific current veins.

56 $\frac{57}{58}$ 485 59 486 [45] Surprisingly, in the upper thermocline, our results do not show a clear and strong 485 enrichment in Nd content. Our hypothesis is that the dNd (dREE) external inputs, likely weathered from the surrounding islands and discharged into the Solomon Sea, are balanced

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487 by the dNd (dREE) removal by scavenging, consistent with the productivity of the area 488 (Radenac et al., 2013; Bonnet et al., 2015). This will be confirmed or disproved with the 489 isotopic Nd signatures.

490 5.2. Interesting features in the dREE profiles

491 [46] This section discusses more specifically the dREE PAAS-normalized patterns and 492 anomalies. Calculated dREE anomalies allow identifying if, after normalization to the PAAS 493 values, an element is enriched or depleted relatively to its neighbors. Thus, they can bring information about the dominant mechanisms affecting the local marine REE pool. Anomalies 495 are calculated following the equations below (Bau et al., 2004; Bau et al., 1996; Friend et al., 2008; Garcia-Solsona et al., 2014). In the following, we will discuss more specifically the La, Ce, Eu and Yb anomalies.

$$
\frac{La}{La^*} = \frac{[La]_n}{3[Pr]_n - 2[Nd]_n}
$$
 (1)
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\frac{Ce}{Ce^*} = \frac{[Ce]_n}{2[Pr]_n - [Nd]_n}
$$
 (2)

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\frac{\mathrm{Eu}}{\mathrm{Eu}^*} = \frac{4 \times [\mathrm{Eu}]_n}{3[\mathrm{Sm}]_n + [\mathrm{D}y]_n}
$$
 (3)
$$
\frac{\mathrm{Yb}}{\mathrm{Yb}^*} = \frac{[\mathrm{Yb}]_n}{2[\mathrm{Er}]_n + [\mathrm{D}y]_n}
$$
 (4)

[47] A complementary parameter to the anomalies is the ratio between normalized LREE and HREE, expressed as Nd_n/Yb_n, which provides information about the slope of the normalized dREE pattern. Figure 7 shows the vertical profiles for the La, Eu, Yb anomalies and the Nd_n /Yb_n slope. Normalization of the dREE to PAAS implies that without any fractionation between the dREE within the water column, the dREE pattern would be flat - Nd_n /Yb_n close to 1- and no anomaly would be observed. The full data set is reported in Table 1. The 506 REE/REE* ratio reveals an enrichment relatively to its neighbors when its value is larger than one, and a depletion in the opposite case.

508 *5.2.1.Dissolved Lanthanum anomaly*

 $\frac{57}{2}$ 521 $\frac{58}{59}$ 522 59 509 [48] All the dissolved Solomon Sea samples collected during Pandora are characterized by positive La anomalies, with values ranging from 3-6 (Figure 7). Such positive values have been 511 observed elsewhere in the ocean and are believed to result from a differential La behavior due to the lacking electron in the 4f shell of the La atom, suspected to increase its stability in seawater, so called the "tetrad" or "double-double" effect (Byrne and Kim, 1990; Byrne and 514 Sholkovitz, 1996; De Baar et al., 1985b; Elderfield, 1988; Garcia-Solsona et al., 2014; Grenier et al., submitted; Jong Hyeon and Byrne, 1993; McLennan, 1994). In particular, while dLa is released from riverine particles when freshwaters are discharged into the ocean, more efficient releasing than scavenging rate could cause local positive dLa anomalies (Lawrence and Kamber, 2006). Nevertheless, the positive dLa anomalies in the Solomon Sea are 519 observed at all the monitored stations even that located far from the coastline. Knowing that the oceanic dREE pattern mostly results from dissolved-particle exchange also occurring in the open ocean (Tachikawa et al. 1999), we are seeking if another factor than the « Tetrad effect » only could govern the La behavior in the Coral and Solomon Seas.

 $\frac{2}{3}$ 525 4526 $\frac{9}{0}$ 530 523 [49] Due to the similar atomic size and close chemical properties of barium and 524 lanthanum, they are suspected to display coupled behavior in seawater (Garcia-Solsona et al., 525 2014; Haley et al., 2014; Grenier et al., submitted). Bishop (1988) and Dehairs et al. (1980) demonstrated that oceanic dBa distribution is governed by the surface biologically driven 527 formation of barite crystal (BaSO₄) followed by its dissolution at depth. Coupling between the 528 two elements could therefore occur if dLa is associated to the dBa/barite cycle within the 529 water column (Dehairs et al., 1980; Garcia-Solsona et al., 2014; Grenier et al., Submitted in 2017; Guichard et al., 1979).

 $\frac{11}{12}$ 531 13 532 $\frac{15}{16}$ 534 [50] Figure 8 displays strong correlations between dissolved dLa and dBa measured on the same samples at all the stations, with $R^2_{\text{coefficient}} = 0.95\pm0.04$. These results support the idea 533 that dLa marine behavior is to some extent coupled to the dBa one. The marked enrichment of dLa over dBa at the « coastal » stations 71, 73 and 77 could reflect the efficient release of dLa from the lithogenic material discussed in Lawrence and Kamber (2006). Nonetheless, the lack of particulate barium data so called as barium excess (Ba_{xs}) prevents us to go farther in discussing the dLa anomaly in the Solomon Sea.

538 *5.2.2.Dissolved Europium anomaly*

25 540 $\frac{26}{25}$ 541 $\frac{27}{28}$ 542 $\frac{30}{31}$ 544 32 545 $\frac{33}{3}$, 546 34 35 547 36 548 $\frac{37}{38}$ 549 [51] A positive dEu anomaly is characterized for all normalized dREE patterns whatever the water mass type and location of the sample. Such positive dEu anomalies were observed in previous studies (Amakawa et al., 2000; Nozaki et al., 1999) but were not discussed till the work of Zhang et al. (2008) and the more recent observations of Grenier et al. (2013; 543 Submitted in 2017). Either on the Kerguelen plateau (Grenier et al., Submitted in 2017; Zhang et al., 2008) or in the Equatorial Pacific (Grenier et al., 2013) these authors invoke a remaining signature of lithogenic inputs of basaltic origin, local basalts being characterized by a positive Eu anomaly. In our studied area, the conspicuous feature of dEu anomaly shows maxima in the surface water, reach a minimum at intermediate depths (\sim 500 m) and then slightly increase again toward bottom except in the Coral Sea profiles characterized by fairly constant dEu anomalies at depths below 1000 m (Figure 7).

 $\frac{39}{10}$ 550 $\frac{40}{41}$ 551 $\frac{43}{44}$ 553 45 554 [52] The higher dEu anomalies (\approx 1.3) at the surface likely reflect relatively recent enrichment of lithogenic origin, which could be of coastal or atmospheric source. Indeed, the 552 Solomon Sea is surrounded by volcanic islands whose basaltic material is enriched in Eu (Grenier et al., 2013). Besides, some volcanoes such as Rabaul, Ulawun and Bagana, are still very active (Lefèvre et al., 2008; Slemons et al., 2010).

 $\frac{46}{47}$ 555 48 556 $\frac{49}{50}$ 557 51 558 $\frac{52}{12}$ 559 $\frac{53}{54}$ 560 55 561 $\frac{56}{57}$ 562 58 563 59564 555 [53] Deeper than 1000 m, the increase of the positive dEu anomaly could result from two 556 non-exclusive processes: i) the release of dREE in intermediate and deep layers caused by the dissolution of basaltic sediments deposited on the margins by submarine weathering followed by the advection of the enriched waters (Grenier et al., 2013; Jeandel et al., 2011; Zhang et al., 2008). As already underlined by Grenier et al. (2013), the preservation of this 560 dEu anomaly is made possible by the fact that the residence time of dEu (320-820 yrs; Alibo and Nozaki, 1999) is larger than that of the thermocline waters across the studied area (10-15 yrs, Fukumori et al., 2004)) ; ii) Grenier et al. (Submitted) suggested that the deep positive dEu anomaly could also result from LREE/MREE preferential scavenging onto surface coating of organic particles in surface water followed by their release at depth (Sholkovitz et al.,

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565 1994). Ongoing measurements of the filtered particles might help to identify the importance 566 of such processes in the Solomon Sea.

567 *5.2.3.Dissolved Ce anomalies*

568 [54] Contrastingly to dLa and dEu, the marked depletion of dCe is observed at all the 569 studied stations although less pronounced in the surface and subsurface waters above 500 m (dCe/dCe^{*} ≥0.4). Consistent with the higher dEu anomalies discussed above, these less 571 pronounced dCe anomalies might reflect recent lithogenic inputs, which are more affecting the upper layers. Higher dCe anomalies (dCe/dCe^{*} ≥0.5) were found mostly in the surface water of stations located around the Solomon archipelago (e.g. stations 42, 43, 60), indicating more recent inputs. Specifically, one upper thermocline sample at station 71 (160 m) shows a significantly high dCe anomaly (-1.4) . However, this station is very close to the coast and was 576 located here to identify any margin input to the waters conveyed by NGCU through the slit between New Britain and Woodlark islands; the existence of strong inputs is thus confirmed by the high positive Ce anomaly observed at this station.

579 *5.2.4.HREE behavior*

23 580 $\frac{24}{25}$ 581 $\frac{25}{26}$ 582 $\frac{28}{39}$ 584 30 585 $\frac{31}{22}$ 586 $\frac{32}{33}$ 587 34 588 $\frac{35}{36}$ 589 $\frac{36}{37}$ 590 $\frac{38}{10}$ 591 $\frac{39}{40}$ 592 $\frac{42}{42}$ 594 43 594
44 595 $\frac{46}{47}$ 597 48 598 51 600 $\frac{53}{54}$ 602 55 603 $\frac{57}{58}$ 605 60 [55] The vertical dHREE profiles show more convex shapes than that of the other dREE (Figure 3). In addition, the Nd_n/Yb_n slopes are increasing below intermediate depths at a rate of two up to the seafloor (Figure 7). Such rapid increase was already observed although not 583 always discussed (Grenier et al., Submitted; Haley et al., 2014; Jeandel et al., 2013; Molina-Kescher et al., 2014). Bertram and Elderfield (1993) noticed that coupling between dREE and dSi cycle could be more significant for the dHREE than for the dLREE and recent works of Akagi (2013) and Grenier et al. (Submitted in 2017) seem to confirm this observation. Here we propose to explore the link between dHREE (represented by dYb) and the dSi cycle in Figure 9. The high values of the correlation coefficients (R^2 = 0.9) support this hypothesis again. However, a break of the slope is observed at around 700 m, the dYb rate of increase diminishing by a factor of 2 below this depth. Although this observation is consistent with that of Grenier et al. (Submitted in 2017), the ΔdYb/ΔdSi slope observed in Figure 9 for dSi concentrations less than 40 μ mol.kg⁻¹ (samples <700 m, Δ dYb/ Δ dSi≈0.09) is larger than that of 593 these authors (ΔdYb/ΔdSi≈0.01). This difference could reflect the impact on both tracer cycles of the different ecosystems characterizing the two areas: the huge diatom bloom on the Kerguelen plateau leads to a dramatic increase of particulate biogenic silica and a 596 subsequent major dSi depletion in the upper layers. Although this scavenging is expected to also deplete dYb, the relative rates of the scavenging processes are likely favoring the dSi subtraction in the Southern Ocean. It is more complex in the Solomon Sea which is known as 599 a hot spot for N₂ fixation due to diazotroph blooms (Ganachaud et al., 2017). Interestingly, roughly 10% of the nitrogen fixed by the diazotroph species was found to be transferred into 601 diatoms leading to a growth of diatom abundance (Bonnet et al., 2016). This moderate diatom growth compared to the Kerguelen diatom bloom is consistent with the higher 603 ΔdYb/ΔdSi ratio observed here. In the deep layers, the observed slope ΔHREE/ΔdSi≈0.04 is 604 consistent with that found in Grenier et al. (submitted) and in the work of Bertram and 605 Elderfield in the intermediate, deep and bottom waters of the Pacific Ocean (See figure 8 of 606 Bertram and Elderfield, 1993).

5.3. Origin of the dREE enrichments in the Solomon Sea

 $\frac{1}{2}$ 608 6 611 $\frac{8}{9}$ 613 $\frac{11}{12}$ 615 13 616 $\frac{15}{16}$ 618 $\frac{18}{10}$ 620 20 621 $\frac{22}{23}$ 623 [56] The preceding two sections underlined several common features indicating that the dNd (dREE) enrichment calculated with our box model (section 5.1) results from the release of dNd (dREE) from the surface and submarine weathering of the surrounding islands. Several complementary parameters allowed us to confirm the nature of this external dNd source and its signature in the dissolved phase. Surface dEu enrichments, larger dCe values are consistent with similar high concentrations observed in the dAl and dMn profiles (Michael et al., 2017). In addition, consistent maxima of dREE, dAl and dMn are also observed at some specific points in the thermocline and intermediate layers (i.e: stations 04-1000m; 10-350m; 20-700m; 42-700 m; 71-300 m; 77-500 m). Such consistencies underline that submarine weathering took place along the island margins since these enrichments could not result from any surface or bottom external inputs. The Solomon Sea is an area of strong internal wave activity and associated mixing (Alberty et al., 2017). It has been suggested that when the continental slope is close to a critical angle, the strong bottom shear velocities enhance sediment resuspension and potential release of chemical elements (Cacchione et al., 2002). Nepheloid layers might result from these processes and be advected further from the slope, contributing to the observed enrichments. The exact location of such resuspension events could be an interesting investigation for future studies.

$\frac{26}{27}$ 625 6 Conclusion

32 628 [57] This study presented vertical profiles of dREE concentrations for 143 samples and 21 stations collected in the Coral and Solomon Seas as part of the PANDORA cruise (boreal summer 2012). Although the profile shapes display common dREE features -i.e surface depleted and enriched at depth- the dREE patterns and anomalies could be discussed and lead to interesting results.

 $\frac{37}{38}$ 632 [58] A first striking result is that, despite the very high dynamic variability of the Solomon Sea, with strong variables currents and recirculations, eddies, internal waves, the REE concentrations are very close to those previously measured at the same locations, confirming the robustness of this chemical family as tracers of continental/ocean exchanges.

 $\frac{43}{44}$ 636 48 639 635 [59] A pronounced dissolved dLa positive anomaly is estimated (dLa*/dLa varying between 3 and 6). The classical interpretation relates to the "tetrad" effect. However, our data show an excellent correlation between dLa and dBa which could suggest a coupling between both elements, lanthanum being associated with the dissolved barium/barite cycle. The particulate La and Ba_{xs} data will likely help to dig this hypothesis farther.

50 640 $\frac{642}{54}$ 643 [60] An europium positive anomaly is also found in all of our patterns with higher dEu*/dEu values in the upper layers. This striking feature agrees with previous observations (Grenier et al., submitted; Grenier et al., 2013; Zhang et al., 2008) and suggests that the enrichment calculated with the box model is lithogenic and of basaltic origin, consistent with the geology of the surrounding islands. The lithogenic source is later confirm by dCe anomaly

645 [61] dHREE behaviour seem to be the most influenced by the Si cycle as suggested by Akagi (2013) and also observed by Grenier et al. (submitted).

 $\frac{9}{0}$ 654 14 657 647 $[62]$ A box model allowed us to establish the net dNd(dREE) fluxes of the waters flowing 648 equatorward through the Solomon Sea. Significant enrichment is observed (F_{total} PANDORA = 649 145.1 \pm 45.8 t(Nd).yr⁻¹) for the Lower Thermocline Layer (between 200-500 m). This 650 enrichment is of main interest, as these waters will eventually be advected till the equatorial 651 eastern Pacific through the lower part of the EUC (Slemons et al., 2010; Grenier et al., 2013). 652 By contrast, the lack of clear net enrichment in the upper thermocline is surprising in this 653 area bounded by continental margins and with many potential sources. This points to the complexity of boundary exchange processes, and to the need of better understanding the 655 removal processes of the oceanic dissolved material. The ongoing analysis of the associated 656 particles and Nd isotopic composition will help to refine and conclude about the robustness of these net exchange fluxes.

7 Acknowledments

 $\frac{21}{22}$ 661 23 662 $\frac{25}{26}$ 664 27 665 $\frac{28}{29}$ 666 30 667 $\frac{32}{33}$ 669 34 670 659 [63] This work is a contribution to the CLIVAR/SPICE and GEOTRACES International 660 programs. We are grateful to the ship crew (RV l'Atalante) who made possible the various in situ measurements, thereby requiring skills and care. The collaboration with SOPAC/SPC, PI-662 GOOS, and University of Papua New Guinea was greatly appreciated. We also acknowledge 663 Dr Benjamin Dupont for his volunteering help during the on-board sampling. The accomplishments were made possible through concurrent contributions of national funding agencies. The Pandora cruise has been co-funded by NSF grant OCE1029487, and by ANR project ANR- 09-BLAN-0233-01 and INSU/LEFE project Solwara (IDAO and CYBER). All the authors whose work contributed to the database GEOTRACES are acknowledged 668 [\(http://www.geotraces.org;](http://www.geotraces.org/) http://www.solomon seaoceanography.org). Besides of that, we would like to thank the research TIM at LEGOS for insightful comment and encouragement. C. Pradoux and F. Candaudap are thanked for their technical support.

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$\frac{50}{2}$ 932 932 **9 Tables and Figures**

$\frac{52}{52}$ 933 53 **Table Captions**

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 $\frac{54}{2}$ 934 55 56 935 Table 1: Location, Depths, Hydrological properties, Ce anomalies, Nd concentration of the analyzed sample in this study and the corresponding water masses identified.

57 58 936 59 937 60 Table 2: Dissolved REE concentrations (pmol.kg $^{-1}$). Data are reported with daily confidence interval (2σ).

938 Table 3 Average dNd concentrations in the different layers of the box model

 $\frac{1}{2}$ 939 3940 $\frac{4}{5}$ 941 Table 4: Water masses and associated volume transport (Sv) at different layer during Pandora 940 (July-August 2012). The water transports were calculated based on S-ADCPs data couple with geostrophic velocities database

$\frac{6}{7}$ 942 **Figure Captions**

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 $\begin{matrix} 8 \\ 9 \end{matrix}$ 943 10 944 13 946 $\frac{15}{16}$ 948 17 949 $\frac{18}{10}$ 950 20 951 21 952 $\frac{22}{22}$ 953 24 954 $\frac{25}{25}$ 955 $\frac{26}{27}$ 956 28 957 Figure 1. General map of the studied area (a) and zoom panel in the Coral and Solomon Sea allowing the identification of the sampling locations (b). The sampling locations are 945 represented by circles and different colors associated with distinct regions. The red circles 946 correspond the Coral Sea and Southern entrance of the Solomon Sea. Samples collected in 947 waters flowing through four straits (Indispensable, Vitiaz, St George's and Solomon), are 948 colorized with dark violet, black, green and dark blue, respectively. These color criteria will be kept all along this work. The main currents flowing in the South Western Pacific Ocean are shown by solid arrow (Grenier et al., 2011, 2013). SEC: South Equatorial Current, NVJ: New 951 Vanuatu Jet, NCJ: New Caledonia Jet, GPC: eastward Gulf of Papua Current, NQC: polarward New Queensland Current, NGCU: New Guinea Coastal Undercurrent, NBCU: New Britain 953 Coastal Undercurrent, NICU: New Ireland Coastal Undercurrent, SSCC: South Subsurface Countercurrent, EUC: Equatorial Undercurrent. The main archipelago and islands are also reported in the map. Along with this, straits are identified by a character covered by red 956 circle: Indispensable, Vitiaz, St.George and Solomon Strait also highlighted in the map as V, G and S, correspondingly.

30 958 $\frac{31}{22}$ 959 33 960 34961 $\frac{35}{36}$ 962 37 963 $\frac{38}{20}$ 964 40 965 41966 $\frac{42}{43}$ 967 44 968 $\frac{45}{16}$ 969 Figure 2. Potential temperature (θ) versus salinity (S) (right) and potential temperature (θ) versus dissolved oxygen (O2) (left) plots for the stations. The curve colors correspond to the different locations denoted in figure 1. The grey curves are representing the same properties at all the hydrographic stations sampled as part of PANDORA. In the left plots, potential density anomaly contours are shown as solid grey lines. Each depth sampled for dissolved REE measurement is identified by a rectangle and its value (m). All the data characterizing the stations represented here are provided in Table 1. The water masses at the sampling depth are also highlighted by their notation: TSW: Tropical Surface Water, SPTW: South Pacific 966 Tropical Water, SPEW: South Pacific Equatorial Water, WSPCW: Western South Pacific Central Water, SAMW: Subantarctic Mode Water, AAIW: Antarctic Intermediate Water, EqPIW: Equatorial Pacific Intermediate Water, UCDW and LCDW: Upper and Lower Circumpolar Deep Water.

 $\frac{47}{40}$ 970 49 971 50 Figure 3. Profiles of dissolved REE concentrations for La, Nd, Eu and Yb. Stations are gathered into five groups with the color codes consistent with their geographical location as proposed in Figure 1.

52 973 $\frac{53}{54}$ 974 55 975 ⁵⁶ 976 58 977 Figure 4. Comparison of our data with those measured in the framework of preceding studies. Yellow points represent data from station SA-7 (sampled during September-October, 1992) located in the middle of the Coral Sea and measured by Zhang and Nozaki (1996). Aqua square, triangle and dot represent data measured at the entrance of Solomon (FLUSEC 22), Coral sea (FLUSEC 43) and at exiting Vitiaz Strait respectively, measured by Grenier et al.

978 (2013). It is noted that all sample using in study of Grenier was sampled in August-979 September, 2006. Sampling date of our samples are reported in table 1.

 $\frac{4}{5}$ 981 6 982 980 Figure 5. dREE patterns normalized to PAAS (×106) at different depths for 8 stations sampled in the Coral Sea and at the entrance of Solomon Sea and for 12 stations located in the Solomon Sea and in the different straits The light colors indicate shallow samples while 983 darker colors represent the deeper ones.

 $\frac{10}{11}$ 985 11 12 986 $\frac{13}{14}$ 987 14 15 988 16989 18 990 19 991 $\frac{20}{21}$ 992 984 Figure 6. a) Schematic description of the Pandora box (red rectangular). The water layer is defined in the table 4. Yellow arrows signify southern input while red arrows characterize output flow through three straits. Meanwhile, colored letters coupled with number indicate different stations together with their transport. E: NGCU transport, N: direct NVJ transport, V, G and S: Vitiaz Strait, St George's Channel and Solomon Strait transports, respectively. b) Enrichment visualizing by simple Pandora box with 2 southern inputs and 3 northern outputs as presented in figure 6a. The Nd concentrations were taken into account here are NdE, NdN in the south and NdS, NdG and NdV in the north. c) Significant enrichment is observed at Lower Thermocline Water, all fluxes are reported in Table 4.

 $^{22}_{22}$ 993 24 994 25 995 $\frac{26}{27}$ 996 28 997 $^{29}_{20}$ 998 $\frac{30}{31}$ 999 Figure 7. Vertical profiles of the anomalies of La (La/La*), Eu (Eu/Eu*), Yb (Yb/Yb*) and of ratio (Nd/Yb)_n, calculated following Bau et al. (2004); Bau et al. (1996); Friend et al. (2008); Garcia-Solsona et al. (2014). The color of markers follow color rule as described in Figure 1. High value was found at the surface water characterize at almost all parameter, except 997 Yb/Yb*. Profile of ratio Ndn/Ybn indicate the recent lilthogenic enrichment at the top of water, then disappear by marine scavenging and later redissolution and or remineralization at depth. Error bars are also plotted together with anomaly value.

331000 34 1001 371003 38_{1004} Figure 8. Linear correlations between dLa (in pmol.kg $^{-1}$) and dBa of all Pandora stations. The relationship confirms the hypothesis that a part of La enrichment comes from the barium cycle in oceanic water (Garcia-Solona et al., 2014; Grenier et al. Submitted in 2017). The slope reflects different rates between Barite formation and lilthogenic dissolution in the water column.

42 1006 431007 461009 Figure 9. Relationship between dYb (in pmol.kg-1) and dSi (in μmol.kg1). Two linear regression point out the strong relation between HREE and Si cycle as suggested by Akagi et al. (2011, 2013) and Grenier et al. (submitted in 2017). The break slope at around 700m suggests the strength of different internal and or external oceanic process on REE distribution.

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(b)

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Figure 2. (continued)

3a) In the Coral Sea, southern entrance of Solomon Sea

Figure 3. Profiles of dissolved REE concentrations for La, Nd, Eu and Yb. Stations are gathered into five groups with the color codes consistent with their geographical location as proposed in Figure 1.

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Figure 5. dREE patterns normalized to PAAS (×10⁶) at different depths for 8 stations sampled in the Coral Sea and at the entrance of Solomon Sea and for 12 stations located in the Solomon Sea and in the different straits The light colors indicate shallow samples while darker colors represent the deeper ones

Figure 5. (continued)

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The Coral Sea, southern entrance of Solomon Sea

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Through Vitiaz Strait

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Figure 7 (continued)

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Table 2: Dissolved REE concentrations (pmol.kg-1). Data are reported with daily confidence interval (2σ).

^altalic values of dREE refer to data with its statistical error bar.

Square brackets indicate data with low recoveries

Table 3: Average dNd concentrations in the different layers of the box model

Table 4: Water masses and associated volume transport (Sv) at different layer during Pandora (July-August 2012). The dNd fluxes were estimated from dNd values compiled in table 3 and water transports entering and leaving the Solomon Sea.

