

Interactive comment on “Physical and remineralization processes govern the cobalt distribution in the deep western Atlantic ocean” by G. Dulaquais et al.

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The two referees are warmly acknowledged for their reviews and constructive remarks on the paper entitled “Physical and remineralization processes govern the cobalt distribution in the deep western Atlantic Ocean”. We are addressing the responses accordingly.

1. General answer to both referees Text: The recommendations to clarify or rephrase sentences, to accord tense, significant numbers and references are taken into account. Introduction: As suggested by Referee#1, it now focuses further on the deep reservoir. Method: Both Referees mentioned the high detection limit when it is calculated as

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[blank] + 3σ [blank]. Instead we now indicate the detection limit using the common definition found in the literature, 3σ [blank], which gives a value of 6.3 pM. The large number of blank analyzes (n=180) slightly increases the standard deviation compared to some others studies. The Referees also pointed out the relevance of the lowest concentrations of apparent particulate cobalt. However total (unfiltered) and dissolved Co concentrations are both significantly higher than the detection limit, and the paired two-tailed t-test shows that the differences between these fractions (e.g., equivalent to apparent particulate Co) are statistically significant at the 95% confident interval ($P < 0.05$, $t_{critical} = 2.84$, $t_{experimental} = 12.83$, $n = 203$). The result of this test is now indicated in the paper. In addition we would like to mention that the comparison between our apparent particulate cobalt concentrations and the truly particulate cobalt concentrations analyzed on particles collected on filters shows an excellent agreement considering uncertainties at the station BATS, except in the nepheloid layer (Phoebe Lam, personal communication). Discussion: Intercomparison: Both Referres mentioned that the crossover stations comparison of dissolved cobalt can be intriguing. However at BATS the surface variability between the datasets can be related to the Co dust deposition, which widely varies in this area as suggested in Shelley et al. (2012). Reversely the best correlation observed at 9°S can due to less dust inputs and margin influence as suggested by Referee #2. The crossover station at 40°S is located on the Malvinas-Brazil confluence. Its position and intensity widely vary with seasons and with the incursion of Subantarctic waters, notably of the Antarctic Intermediate Waters and Circumpolar Deep Waters. Those seasonal variations can explain the differences of dissolved cobalt concentrations observed at intermediate depths between the dataset of Lohan et al. recorded in January 2012, and our dataset from March 2011. In the deepest waters, the difference observed in the nepheloid layer can be due to differences in the resuspension/dissolution of benthic sediments. Despite differences, the three comparisons show that ranges of concentrations are in the same order of magnitude and allow comparison between the different datasets. These comments are now added in the paper. Remineralization in the ACW: The depths of the mean dissolved

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cobalt concentrations in the Atlantic Central Waters were not reported correctly (at page 15975-line 15), introducing confusion, so it is now corrected with the right depths (150-800 m).

2. Specific answer to Referee #1 "My suggestion here would be to make a budget table or/and a scheme which would made the synthesis of all the fluxes calculated to help the reader. This would also allow to remove a part of the calculations explanations from the text and make the reading easier." A conceptual scheme representing the Atlantic circulation and the concentrations of dissolved cobalt in the different water masses is now added, as Figure 7.

"It would be really nice to add more general thoughts about how each described processes interplay with the global biogeochemical cycle of cobalt in the ocean." The different processes are described and quantified in the deep and intermediate reservoirs, as well as the role of the dynamic structures and the vertical diffusion as they may provide a link between the deep and the surface distributions of DCo. The interplay of the physical and remineralization processes with the intermediate and deep distributions of DCo are thus described at the scale of the Atlantic. The processes and the biogeochemical cycles of DCo in surface waters along the section will be described in another paper (Dulaquais et al., in prep.).

"Abstract L25: "dilution and mixing": dilution can be a consequence of mixing but it is not a process by itself" Corrected by "dilution due to mixing processes"

"1/Introduction P15953, L23-27: unclear, how oxidation can occurs in anoxic conditions?" The sentence is now removed.

"P15954, L9-20 and P15955, L5-8: these two paragraphs should become one and the authors should discuss why these findings can be important in the context of the present study." The introduction has been rephrased and those considerations are now included.

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"2/Methods P15955, L18-20: what was the time of the year for leg3 and leg4?" Added

"P15957, L23-24: "Bown et al., 2011" not 2010" Corrected

"DCo and PCo concentrations shown in this study are corrected with their respective reagent blanks", already mentioned line 20". Deleted

"P15962, L16: The highest value reported here, 93.27 ± 3.31 pM, is somehow out of range considering the 0-75 pM range for standard Co addition" The range of the standard Co additions was not reported correctly, the highest addition was indeed 100 pM. This is now corrected.

"PCo has already been defined in the method section". Deleted

"P15963, L21: "locate" should be written "located"" Corrected

"P15964, L6-8: adding the numbers of events and run a P test would strengthen the main statement of this sentence ("strongly correlated")" These values of $n = 57$ and $P < 0.05$ are now added into brackets

"P15965, L4-15: would this paragraph have been more useful in the general introduction?" As suggested by the Referee, this paragraph is now partly used in the introduction

P15966, L5 to P15967, L2: UV treatment step might be crucial as well regarding significant differences observed between DCo measurements made by different labs. By this I mean that the UV lamps characteristics and the UV system device can be more or less efficient. Do the authors have also an idea about the Co extraction recovery prior to ICPMS compared to the pre concentration step during FIA-chem. analysis? The UV-devices can indeed be more or less efficient, hence the recovery of the DCo concentration can change. However analyses of the reference material (SAFe and GEOTRACES seawater samples) show that our method is in the range of the consensus values obtained by different methods, UV-systems and analysts (Table 1).

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“P15966, L19: remove “for” “ Corrected

“P15971, L27: remove one of the “the”.” Corrected

“P15974, L17-L19: previous section begins with the same observation” Deleted

“P15976, L4-5: “In intermediate and deep Waters...mesopelagic waters”, please rephrase”” The sentence has been rephrased

“P15977, section 4.4.1, any reasons why surface waters are define as the 0-150 m layer?” This is the depth mostly impacted by the geostrophic currents, as now defined in the paragraph 4.3.2. Furthermore it is also where significant DCo gradients were occurring. By vertical diffusion and lateral advection that increases the turbulence, DCo can be injected into this surface layer. Those considerations will be discussed in details in another paper focusing on the surface waters (Dulaquais et al., in prep.).

“P15981, L16-23, it is also important to mention that eddies and vertical diffusion could both acts as Co sources” This was already mentioned in the text (“eddies and dynamic structures . . .role in the fertilization of the surface water in DCo. . .”).

“P15982, L13-15, this statement has already be written at the beginning of the conclusion” Deleted

“Table 3: PCo concentrations, considering the standard deviations reported here, the variability of PCo concentrations seems to be high in each water layers considered, is this mainly due to the uncertainties of the measurements? Probably, because concentrations are much lower than the detection limit.” As mentioned here above, the detection limit is now re-calculated with the common definition and the measured dissolved and total Co concentrations were well above it. The paired two-tailed t-test also shows that the differences between the total and dissolved fractions (e.g., equivalent to apparent particulate Co) are statistically significant at the 95% confident interval ($P < 0.05$, $t_{critical} = 2.84$, $t_{experimental} = 12.83$, $n = 203$). Thus the relatively high standard deviations on the mean PCo can be further due to the variability in the particulate

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matter concentrations and their Co composition.

“Figure 2: dissolved oxygen (O2) instead of O₂” Corrected

“Figure 3: legend on each nutrient vertical section (reported as PO₄, NO₃, SiO₂) should be consistent with the description made in the methods section (Phosphate (HPO₄²⁻); Silicate (Si(OH)₄⁻); etc)” Corrected

“Figure 5: error bars should be added on DCo and PCo vertical profiles.” The error bars have not been added to the figure for a better reading. But the standard deviations on the measurements will be available in the datasets on the bodc.uk website.

“Figure 5 Axis numbers and dots should be a bit bigger” Corrected

“Figure 6: Axis numbers and dots should be a bit bigger.” Corrected

“Any ideas on what could explain that the weakest correlation is observed for samples that have been analysed with the same technique ((f) FIA-Chem; data comparison between Lohan et al., and Dulaquais & Boye)?” An explanation is proposed as indicated here above.

“Figure7: I have the feeling that this figure is not really usefull, is it?” This Figure is replaced by a conceptual scheme, and it is now in a supplement material. It is indeed an important figure to show the meridional gradients of DCo in the deep waters.

“Figure 8: Axis numbers should be a bit bigger.” Corrected

3. Specific answer to Referee #2 “The crossover stations comparison is intriguing. These data suggest a combination of temporal variability in cobalt distributions at BATS and the deep South Atlantic, and I also think potentially the detection of different physiochemical fractions by the different methods used. It might be worth suggesting this in the text. Might it also be worthwhile to mention that the South Atlantic crossover station might experiences less temporal variability due to lesser dust input or coastal influences, potentially allowing for better agreement when comparing methods at this

C8203

station relative to the other two? It is great to see these datasets being compared and discussed and it highlights the complexity of cobalt and cobalt speciation, encouraging more critical thinking about what physiochemical fractions are observed with a given method.” We thank the Referee for these comments. They are now included in the text (as indicated here above)

“The discussion of the Iceland volcanic eruption as an explanation for the 20 pmol/kg increase in NADW is intriguing, though perhaps more care could be made in considering the fate of the dissolved flux of cobalt after seeding by the ash. In the Frogner study, the dissolution rates decreased precipitously within an hour and it seems a bit remiss to me that there was no discussion here of the potential removal of cobalt post-eruption, or how a decreased release might change the effective flux of cobalt to the water column. Could the authors perhaps address their assumptions a bit more clearly here?” The decrease of the dissolution rate does not change the effective flux because the release from the ash (8.76 nmol of Co release per gram of tephra) is a cumulative release. The mean input of DCo we estimated from the ash ($16.3 \pm 6.3 \mu\text{mol.m}^{-2}$) is in the same order of magnitude than the excess of DCo we measured ($25.6 \pm 6.3 \mu\text{mol.m}^{-2}$). Furthermore the transit time of 2 years of the NADW fits with the excess of DCo being detected 2 years after the eruption. These observations strongly suggest that the volcanic eruption can be a source of DCo that has been advected in the core of the NADW. Because of the quick release of Co from the ash, and probably because of the short residence time of these particles in the surface waters, it is possible that most of the input of DCo occurs under the ash plum. Its advection by the NADW can then enhance the concentration of DCo far away from the eruption, similarly to the advection of DCo from continental margins. These considerations have been added in the text.

“How did the authors obtained the 8.76 nmol Co release value?” The value is obtained from the figure in Frogner et al. (2001). It shows that after 45 minutes 8.74 nmol of Co per gram of tephra is released in natural seawater. After 1.5 hours the release is 0.02 nmol of Co per gram, after which it can be considered negligible. So the cumulative

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release of Co is 8.76 nmol of Co per gram of tephra after 1.5 hours. It is now mentioned in the text.

“I am skeptical of the explanation that preferential remineralization of P to Co calculated in the upper 400 m accounts for the decoupling of Co and P in deep waters and that deep scavenging is not occurring. Much of remineralization generally occurs in the upper hundreds of meters, so I am confused by the calculations in the upper water column here being applied to explain deep-water decoupling. Could the authors clarify this, perhaps by more clearly stating depth ranges over which they choose to make this claim and why? I think it is also important to keep the timescales of scavenging in mind. If scavenging were not occurring, wouldn't we expect the cobalt profiles to look like N and P? I don't disagree that scavenging may be slow relative to the timescale of circulation within the deep western boundary current, but I think it is valuable to contextualize the conclusions here within an appropriate timeframe.” We have now re-phrased this paragraph for a better reading and clarity. We also re-calculated the percentages of DCo and P produced by cumulative remineralization in: - the surface waters impacted by the geostrophic currents (0-150 m), - the upper-ACW imprinted by the North Brazil Current (150-400 m), and - the lower-ACW fed by the Central South Equatorial Current (400-800 m). Our data shown that there was no significant correlation between DCo and P in intermediate and deep waters, suggesting a decoupling between those parameters. Furthermore the overall lower DCo:P ratios we recorded in deep waters compared to the surface, and the increase with depth of the Co:P ratios in particles (Sherrell and Boyle, 1992), both suggested that the decoupling can be either due to preferential remineralization of P relative to Co, or preferential scavenging of DCo. Our measurements shown, however, that there was no increase in PCo with depth, suggesting that scavenging processes may be negligible. Furthermore our estimations of the cumulated remineralized P and DCo shown a much higher increase of remineralized P with depth relative to DCo, further supporting the hypothesis that preferential remineralization of P can largely cause the decoupling between DCo and P in deeper waters. The decoupling does not imply that DCo should have a scavenged-type dis-

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tribution. Indeed, actually the strongest remineralization of DCo occurs deeper than that of P (Table 3), probably also leading to the decoupling. Timescales of the different processes would have been indeed useful to strengthen our conclusions. These comments are further included in the text and the Table 3 has been modified accordingly.

“The authors argue that the presence of organic ligands justifies negating scavenging in the deep waters. I would agree that complexation likely slows the scavenging process, but we have found that cobalt binding ligands are often not in excess of the total cobalt beneath the euphotic zone, presumably leaving the labile fraction susceptible to scavenging. Labile cobalt often displays intermediate water maxima and seafloor minima in the open ocean. This would suggest that deep waters inherently carry a composition of cobalt that is highly complexed relative to overlying waters, or that, along the circulation path and from raining particulate matter from above, labile cobalt in deep water is lost to scavenging over time. In the Ross Sea, we observed rather high concentrations of labile cobalt that we’ve attributed to the virtual absence of cyanobacteria in that cold environment, which have been demonstrated to produce cobalt-binding ligands (Saito et al. 2010). If Antarctic waters are generally characterized by higher labile and total cobalt, and that water feeds the deep South Atlantic, (where lower total cobalt is observed as observed in this manuscript, and where we have also previously observed low labile cobalt/high % complexation (Noble et al. 2012)), it suggests to me that scavenging has occurred along this trajectory or from above, presumably removing the labile fraction. I would agree that scavenging of the complexed fraction should be significantly slowed, but it may affect the labile fraction. “ The Antarctic water-masses flowing in the southwestern Atlantic - the AABW formed in the Weddell Gyre (11 Sv, Kerr et al., 2012), the AAIW entering from the Drake Passage, and the CDW (upper and intermediate components) - all dispatch high levels of organic complexation of DCo (>75%->90%; Bown et al., 2012). Thus the advection of DCo in these waters occurred predominantly in the organic forms, hence the organic complexation might be promoting the solubilization of DCo along large-scale transportation (Bown et al., 2012). A relatively higher proportion of inorganic Co (up to 25%) can be found in the UCDW

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characterized by rather low oxygen content (Bown et al., 2012). But it was argued that the low temperatures in addition to the low O₂-content may have promoted the stabilization of the more soluble inorganic Co(II) species in the UCDW, still preventing DCo from being scavenged (Bown et al., 2012). Furthermore the DCo in the UCDW dispatch similar concentrations in the southwestern Atlantic (58.7 ± 3.9 pM n =4, this study) compared to the zero meridian (57.3 ± 2.18 pM n =14, Bown et al., 2011), further suggesting stabilization of DCo along UCDW advection. At the bottom the DCo concentrations increased northward and there DCo was almost fully complexed by organic ligands (Bown et al., 2012). The situation might be different in the Ross Sea as suggested by the Referee, but this would mainly impact the advection of DCo in the Pacific. The DCo concentrations in the UCDW are now reported in Table 2, but not these comments. We are indeed awaiting for the completion of the analyses of the organic complexation of DCo, before discussing its impact on the distribution of DCo in the West Atlantic. Instead, the sentences referring to the organic complexation were most often removed from the text.

“As such, I don’t think that invoking scavenging in the deep ocean while also invoking complexation as a means to protect cobalt from scavenging is a paradoxical statement (pg 15967 line 13).” The sentence has been changed by modifying “is paradoxical” by “contrasts with”.

“I am also wary of leaning too hard on conclusions drawn from the apparent particulate cobalt (specifically with respect to scavenging) when the values are often close to the detection limit, especially when the values being compared are below the detection limit (i.e. Table 3).” As explained here above the paired two-tailed t-test shows that the differences between the total and dissolved fractions (e.g., equivalent to apparent particulate Co) are statistically significant at the 95% confident interval ($P < 0.05$, $t_{critical} = 2.84$, $t_{experimental} = 12.83$, $n = 203$).

“These would benefit from at least a couple key station labels, particularly ones explicitly mentioned in the text and in references to these figures.” Key-stations are now

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labeled on Figures 2,3,4

“Pg 15953, line 20 – the wording “unfavorable microbial oxidation” is confusing. Perhaps a clearer phrasing would be “slowed microbial oxidation” “ Corrected

“pg 15961 line 6 – should read “relatively” rather than “relative” “ Corrected

“pg15961 line 19 – please insert reference to Fig. 3” Corrected

“pg15961 line 24 – typo - “diazotrophic” “ Corrected

“pg15961 line 26-27 – please correct for tense agreement” Corrected

“pg 15962 line 2 - should read “relatively” rather than “relative” in general” Corrected

“please use consistent wording for nutrient distribution/nutrients distribution/nutrient distributions “ Corrected

“pg 15692 line13 – should read “other” rather than “others” “ Corrected

“pg 15963 line 21 – should read “located” rather than “locate” “ Corrected

“pg 15964 line 14 – should read “PCo>5pM” rather than “PCo<5pM”” Corrected

pg 15965 line 11 – I would be careful of the wording “no scavenging process” here. It does not appear to be detected although it is a process that occurs, so perhaps this could be worded more carefully by saying it is slow or is not apparent relative to the timescale of water mass circulation. The sentence has been deleted as this paragraph, as recommended by Referee#1.

“pg 15966 line 21 – should read “Fig. 6e” rather than “Fig. 10e” “ Corrected

“pg 15967 line 9 – should read “This leads to the hypothesis [that] there is no: : .”” Corrected

“pg 15967 line 12-13 – please adjust the definition of hybrid-type metal to include both nutrient-like and scavenged-like behavior (hence the term “hybrid”). As it currently

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reads, a hybrid-type metal has the same definition as a scavenged-type element.” Corrected as “. . .or the hybrid-type metals, those elements that have a nutrient behavior in surface waters and are strongly influenced by scavenging processes in the deep waters (Noble et al., 2008)”

“pg 15967 line 19 – The 2012 paper argues that mixing could describe the features observed within the OMZ, not the deep waters.” Corrected as “poor oxygenated waters”

“pg 15968 – lines 10-15 - It is interesting to see the increase in PCo in deep waters and evidence of benthic remobilization of cobalt. Might it be worthwhile to include transmissiometer data if that is available as it would further support this argument?” Transmissiometer data will be available with the NIOZ-dataset, and the good fit between the increase in transmissiometry and PCo near the bottom is now mentioned in this part.

“pg 15968 lines 23-25 - In the discussion of dissolved concentrations between the Western North Atlantic and southeastern atlantic, it would be useful to add the Bown et al. 2011 data to the table in order to make this point clear regarding excellent agreement, as the reader should not have to look up another paper in order to see this. “ The data of Bown et al. (2011) are added to Table 2

“pg 15969 line 5 and 20 – I don’t think isopycnes is an English word. Perhaps isoclines, isopleths, or isopycnals?” Corrected into “isoclines”

“pg 15971 line 7 – should read “increased by 20.5” rather than “increased with 20.5”” Corrected

“pg 15971 line 8 – it would help the reader if important station labels were added to Figs 3, 4, and 5. Perhaps also add the year for leg 1 - I think this would help to compare it in time to the 2012 leg 4. “ Key stations and years are added on Figures 2,3,4

“pg 15971 line 19 – should read “graphite” “ We meant granite (corrected).

“pg 15972 line 3 – “Anyway” is colloquial and I would suggest removing it.” Deleted

C8209

pg 15974 line 8/9 – incomplete sentence The sentence and paragraph have been rephrased for a better reading.

“Saito et al. 2004 nor Noble et al. 2008 are not applicable references here and should be removed from this statement.” The sentence has been rephrased (and the references uploaded) to indicate that relatively high DCo were previously observed in low oxygenated waters.

“pg 15976 line 4 – I believe Bown et al. 2011 also looked at Co:P ratios – might be nice to add this reference here. We also compared Co:P in the Noble et al. 2008 paper.”
References added

“pg 15978 line 21 –should read “indirect” rather than “undirect” “ Corrected

“Noble et al. 2008 could be cited here as this work studied Co cycling in eddies off Hawaii.” Reference added

“pg 15979 line 3 – should read “estimated to be negligible” rather than “estimated negligible”” Corrected

“pg 15980 line 23-26 please rephrase this sentence to make it clearer.” The sentence has been rephrased.

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