To the editor,

We are grateful for the time and effort extended by both anonymous reviewers, whose close attention to detail in reviewing our manuscript makes their praise all the more meaningful.

Both reviewers identified a need for clarity in structuring the results and discussion section and better ordering of figures (and where/when they are referenced in the discussion). To remedy this, have split our results section into 3 subsections, and our Discussion section now contains 10 subsections. We have also added an introductory paragraph at the start of the discussion that outlines the upcoming discussion in a logical order. We hope that this new ordering of the manuscript will assist readers in approaching this large manuscript. A great deal of care has also been taken to make sure figures are not referenced out of order, which was an annoyance to both reviewers.

Furthermore, the discussion of coastal cobalt sources has been modified to reflect an ambiguity in the actual source mechanism outlined in Reviewer 2's comments. We have added discussion, particularly in lines 620-626 and 699-708, which acknowledges the lack of mass balance between Mn/Al accumulation rates off Peru and diffusive Mn fluxes out of the sediments. We have also clarified our language to present this source as "coastal" rather than "sedimentary", so that the ambiguity of the Mn and Co sources is preserved.

We have also reorganized the conclusion section, as recommended by reviewer 2, so that figure 14 can be used as a guide to the summary of the data presented in the Results and Discussion sections.

Below, we describe changes in the new manuscript from both Reviewers' line comments. The line in the full-markup draft is present in parentheses. Additional changes to the manuscript are largely to make sentences more easily understood, and, with the exception of the description of the coastal source section, none of the conclusions have been altered.

Sincerely,

Nick Hawco and Mak Saito

Reviewer #1

Line 57. I'm not sure you can definitively say that Co is the least abundant inorganic nutrient, Cd is similarly in the same range, I'd say, "one of the least"

(59) This has been replaced. However, while surface Cd concentrations are extremely low, the mean oceanic Co concentration is significantly less than Cd, see Moore et al. 2013.

Line 64. which suggests. . .

(66) This has been changed.

Line 88. 100 pM – the space between the value and unit is missing. This error occurs frequently, but not every time. I have not listed this observation where it occurs later in the text.

(91) This has been changed, and we have made our best attempt to correct similar mistakes throughout the manuscript.

Line 170. Include the resistivity of the Milli-Q water here. As Milli-Q is a brand name it might be better to say ultrahigh purity water, or something similar, instead of Milli-Q

(174) This has been changed, and other references to Milli-Q water have been substituted with 18 MΩ water. See lines 179, 212, 213.

Line 145. Delete " is measured"

(149) This has been deleted.

Line 203. 1.5 mL of 1.5 M sodium nitrate

(207) This has been changed to better separate the volume and the concentration of reagents. However the reagent is nitrite, not nitrate.

Line 215. Broader than what? Just "broad" will do, perhaps with the range of tested concentrations stated.

(219) Broader has been changed to broad.

Line 216. Replace "deviation" with "variance"

(220) This has been changed.

Line 234. in the lab

(239) "the" has been added to this line.

Line 253. You should probably include the initials: C. Parker and K. Bruland

(259) We have added initials.

Line 281. What was the ratio of HCl: NHO3: HF?

(285) The concentrations of the individual acids have been added. For reference the ratio is 1:1:1, which is clearer in the new version.

Fig. 4. I think it would help the discussion to add some station numbers to this figure

(Fig. 4) We have added station numbers that appear in figure 1 to the top of the sections in Figure 4. We have done the same for figure 6.

Line 351. Baars and Croot (2015)

(365) This mistake has been corrected.

Line 410. You shouldn't really be referring forward to Figure 13c here. This needs some rearranging so that you are not referring forward. You could simply use the values without referring to Figure 13c until later in the text. There are a number of instances that you are

referring to figures that haven't been described yet, which you should try to avoid as much as possible

(341) We have removed the reference to this figure here. For this version of the manuscript, we have worked hard to avoid the need to reference figures out of order and have reworked the layout of both the results and the discussion section to achieve this.

Line 445. ". . .new cobalt sourced from the shelf is rapidly incorporated into biological cycling and that the capacity for phytoplankton Co uptake. . ." - the biological cycle, or biological cycles

(485) this phrase has been changed to "the biological cycle"

Line 502. delete "in the"

(546) This error has been fixed.

Line 527. Is there any documentation of reducing sediments on the South American continental shelf that could support your assertion?

(573) We have removed reference to the reducing sediments in this sentence. Due to similar comments from Reviewer 2, we have added an additional paragraph discussing source mechanisms in detail (Lines 611–626) that makes better use of the existing literature in documenting reducing conditions on the Peru shelf, including the Scholz et al. 2011 GCA study.

Line 544. Consistent with release

(618) "with" has been added

Line 547. Is this sentence reversed? ". . .sedimentation outpaces dissolution of Co and Mn only in very shallow water columns and/or proximal to input, which explains the lack of dissolved benthic maxima for both elements beyond Station 2". If sedimentation outpaced dissolution of Co and Mn in shallow water/close to source, then wouldn't we expect to see no benthic maxima?

(611-626) To avoid unnecessary confusion to the reader, we have deleted this sentence. Reorganization of this section has largely been to acknowledge that, while a margin cobalt source is certain, its mechanism is unclear. In addition to rewriting this paragraph, we have also added a new paragraph (Lines 698-707) that highlights this uncertainty more explicitly.

Line 603. As I understood the Noble et al (2012) study, the dCo and LCo plumes were extensive, but the dFe plume was much smaller and the dMn plume wasn't evident, at least in the ODV plot, although they do argue for a sedimentary source for all three elements, explaining the differences in plume areal extent by preferential scavenging of Mn>Fe>Co. This sentence needs rewording to reflect this.

(694) We have rewritten this sentence so that it is solely focused on the Co plume. For the scope of this section, the main importance is that both the South Pacific and South Atlantic have OMZ plumes of dCo and both regions have depleted Co contents in shelf sediments, suggesting that the same mechanisms is acting in both basins.

Line 619. 20 μM dissolved O2

(722) This has been changed.

Line 627. This is also consistent with Sholkovitz and Copland (1981) who estimated that 97% of Co escapes from freshwater systems (Sholkovitz, E.R., and Copland, D., 1981. The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in river water. Geochimica et Cosmochimica Acta., 45, 181-189.)

(96) We have added this reference to the introductory paragraph describing coastal Co sources (Line 96). While this is a very relevant study, in light of the uncertainty in the actual source mechanism we found it more appropriate in the introduction than in the discussion.

Line 683. counterpart?

This has been changed.

Line 701. Or they can access the Co from the particulate pool? Is there any evidence for this in the literature?

(811-813) We have modified this sentence to explicitly refer to the particulate pool. Due to the low abundance of Co in dust and the extremely low dust supply to the south pacific, we interpret the particulate Co in the surface ocean (Fig 6c) to reflect Co bound in biomass. We therefore interpret the high pCo:dCo ratio in the South Pacific gyre to reflect recycling between Co-bearing biomolecules as the plankton biomass turns over, rather than the existence of an unexploited, additional resource (such as dust).

Line 706. Prochlorococcus produce ligands too. Might be worth mentioning this as you say that the Prochlorococcus abundance was high

(820) We added a mention to this observation.

Line 729. Delete "of"

(843-44) This has been changed to "in the Peru upwelling region"

Line 764: fluctuates

(893) This has been changed.

References. Check your references as some of them are not displayed properly, e.g. Baxter et al (1998), Line 807, and there are some instances of extra, inconsistent punctuation.

(938) We have corrected the Baxter et al. reference and have tried to correct similar errors in formatting.

Specific responses to Reviewer #2

Title: The paper contains many more interesting observations (and corresponding interpretations) than just the Co plume in the oxygen minimum zone. Consider a more general title that fully captures the comprehensive character of the presented data set.

After much thought, we have decided to keep the shorter, succinct title of the manuscript. Almost all of the observations are focused around the oxygen minimum zone and the processes supporting the cobalt plume therein. We have tried to emphasize the role of the OMZ plume in Cobalt biogeochemistry in the first paragraph of the discussion section, which have been added since review (Lines 396-419)

Line 47, abstract: Add 'in' before 'oligotrophic regions'.

(47) This has been added.

Line 72: It would be useful to define labile Co and the abbreviation LCo here.

(75) We have moved up the definition of LCo as suggested.

Line 75: Does it matter whether the Mn oxides are formed by bacteria or abiotically? I assume they would be enriched in Co either way (see also Line 497).

(78) We have changed 'bacterial' to 'authigenic.'

Results section: The Results section would be easier to follow if it was divided into subsections, e.g., vertical Co profiles, lateral Co distribution, etc.

We have split the results section into 3 major subsections discussing the distribution of dCo (300), pCo (347), and LCo (362).

Line 293: Add number of gyre station so that it can be easily identified in Figure 3.

(305) Stations plotted in figure 3 have been added in parentheses. Per a comment from Reviewer 1, we have also added station numbers to figures 4 and 6.

Line 299: 'overturning' (typo).

(310) Corrected.

Line 313: Add reference to figure.

In order to avoid for referencing figure 10 out of order (an issue raised by both reviewers), we have not made this change. However, we have marked Station 2 on both figures 4 and 6 (and figure 1) to make it easier for a reader to understand.

Line 321: Upwelling of P-rich and O-poor water 'results' in high dCo? Rephrase for clarity.

(333-335) We have rewritten this sentence for increased clarity.

Line 329: Figure 13?

(342) We have removed reference to this figure.

Line 340: Add figure reference.

 Will add.

Line 359: "On the GP16 transect . . .".

(353) This has been added.

Line 417: I assume you mean "low O2/high dCo water masses mix with high O2/low dCo water masses". Rephrase for clarity.

(452-453)This sentence has been rewritten to make its meaning more clear.

Line 424: Is the LCo:O2 trend shown in the figures? If yes, add figure reference; If no, C3 add 'not shown'.

(460) 'not shown' was added.

Line 433: What is meant with "double 0 µM intercept"? 2 x 0 µM? Rephrase for clarity.

(469) This has been rephrased. The word "twice" has been substituted for "double" in the original manuscript, which was the main cause of confusion.

Line 434: What exactly resembles "profiles of N2 . . ."?

(471-476) The wording of this sentence has been redone. It has been emphasized that the dCo profile is what is similar to the excess N2 profile.

Line 444: The 50 m depth range is not shown with separate symbols in Figure 5c. Later in the text other depth ranges are discussed which are not shown either (Line 457). I suggest adding more color codes to Figure 5c to indicate all the depth ranges and corresponding covariation trends discussed in the text. Otherwise the discussion is difficult to follow.

(485) We have modified figure 5 so that the 0-50m depth range is presented as cyan, and the 50-200m depth range is presented as blue. Specific references to the colors in figure 5 and also figure 9 have been added parenthetically (also Lines 498, 499, 503, 535, 541, 547, 554, 556…).

Line 492: What is meant with 'redox barrier'? Do you invoke a biological process or just that Mn oxides do not form at very low oxygen concentrations?

(536) We have rewritten so be more specific, mainly highlighting the thermodynamic and kinetic basis for a sensitivity of Mn oxidation to changes in O2 concentration.

Line 499: Figure 7C does not show pCo.

(545) We have changed to figure reference to 6C.

Line 502: Remove 'in'.

(547) This has been changed.

Line 518: Figure 14 is a summary figure which has not been introduced at this point of the discussion. I recommend referring to actual data here and to restrict references to Figure 14 to the Conclusions section.

(563) We have removed the reference to figure 14, both here and everywhere else, with the exception of the conclusion section, which has been reorganized. For the purposes of this sentence, we have added a reference to figure 5c.

Section 4.3: See comment above on reductive Mn dissolution in the water column.

(620-627) We have incorporated the conclusions from the Scholz et al. 2011 study more explicitly in this section, and in the next (Lines 699-708). We have backed off of the wording on sedimentary sources, instead using "coastal" as a kind of catch-all until more details about the nature of this source come to light.

Line 545-549: The Peruvian shelf occasionally experiences oxidation events which also favor Mn deposition and burial (see discussion in Scholz et al., 2011).

(682-684) We have added a sentence making explicit mention to this effect.

Line 590: "oxidizing conditions . . . prevent reductive dissolution . . ." is a misleading statement. The sediments at the western Pacific margin are certainly Mn-reducing in the shallow subsurface but the oxic surface sediments prevent diffusive escape of the pore water Co and Mn into the water column.

(677-678) We have clarified our hypothesis here, emphasizing that oxidizing conditions limit the release of Co from the sediments, as point out in the above comment.

Line 594-Line 606: Because of low water exchange kinetics, Co is incorporated into pyrite and does not tend to from its own sulfide minerals (Morse & Luther, 1999, GCA 63, 3373-3378).

(685) We have have made note of this distinction and have modified our language accordingly. The Morse and Luther citation is added to Lines 688-689.

Line 613: Does 'crust' refer to 'andesite' in this equation. It does not matter what you take but it should be consistent throughout the manuscript.

(722) The range in calculated fluxes represents calculations from both upper continental crust, as defined by McLennan 2001, and Andesitic endmembers, as defined by Taylor and McLennan 1995).We have tried to make this more explicit in the paragraph by indicating this in parenthesis, as well as an additional reference to table 2.

Conclusions: I really like Figure 14 and therefore recommend to introduce it more explicitly at the beginning of the Conclusions (something like: "the major pattern and underlying processes identified in this contribution are summarized in Figure 14"). The major finding can then be summarized by guiding the reader through Figure 14.

(853) We have reorganized the conclusion section, as suggested, by way of examining figure 14. The ordering of the summary follows an approximate 'source-to-sink' direction which can be followed along in figure 14.

Caption Figure 1: What depth or potential density do the isolines correspond to? This represents oxygen at 300m, which was accidentally omitted from the caption.

(1205) We have added that the O2 data comes from 300m.

A dissolved cobalt plume in the oxygen minimum zone of the Eastern Tropical South Pacific

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Abstract. Cobalt is a nutrient to phytoplankton, but knowledge about its biogeochemical cycling is limited, especially in the Pacific Ocean. Here, we report sections of dissolved cobalt and labile dissolved cobalt from the US GEOTRACES GP16 transect in the South Pacific. The cobalt distribution is closely tied to the extent and intensity of the oxygen minimum zone in the eastern South Pacific with highest concentrations measured at the oxycline near the Peru margin. Below 200 m, remineralization and circulation produce an inverse relationship between cobalt and dissolved oxygen that extends throughout the basin. Within the oxygen minimum zone, elevated concentrations of labile cobalt are generated by input from coastal sources and reduced scavenging at low O_2. As these high cobalt waters are upwelled and advected offshore, phytoplankton export returns cobalt to low-oxygen water masses underneath. West of the Peru upwelling region, dissolved cobalt is less than 10 pM in the euphotic zone and strongly bound by organic ligands. Because the cobalt nutricline within the South Pacific gyre is deeper than in oligotrophic regions in the North and South Atlantic, cobalt involved in sustaining phytoplankton productivity in the gyre is heavily recycled and ultimately arrives from lateral transport of upwelled waters from the eastern margin. In contrast to large coastal inputs, atmospheric deposition and hydrothermal vents along the Eastern Pacific Rise appear to be a minor sources of cobalt. Overall, these results demonstrate that oxygen biogeochemistry exerts a strong influence on cobalt cycling.

1. Introduction

Cobalt is one of the least abundant inorganic nutrients in seawater and its scarcity may affect phytoplankton growth in certain regions (Moore et al., 2013). In the high macronutrient waters of the Costa Rica upwelling dome, for instance, Co and iron (Fe) amendments to surface seawater increased phytoplankton production more than Fe alone, promoting growth of the cyanobacterium *Synechococcus* (Ahlgren et al., 2014; Saito et al., 2005). While eukaryotic phytoplankton mainly use cobalt to compensate for insufficient zinc (Sunda and Huntsman, 1995), populating the same enzymes with either metal (Yee and Morel, 1996), marine cyanobacteria have an absolute growth requirement for Co that cannot be substituted, which and suggests they may be more prone to limitation (Saito et al., 2002). Yet, the extent to which their

68 growth *in situ* is affected by cobalt scarcity ultimately depends on the processes that add Co to,

69 or remove it from, the surface ocean relative to other limiting nutrients.

70

71 Biological cycling of dissolved cobalt (dCo) is apparent in vertical profiles, showing uptake and

72 export in the surface and regeneration in the thermocline (Bown et al., 2011; Dulaquais et al.,

73 2014a; Noble et al., 2012). While dCo in the euphotic zone can be entirely bound by strong

74 organic ligands, a substantial portion (10–50 %) of subsurface dCo is unbound and labile

75 (LCo10–50 %, Bown et al., 2012; Ellwood and van den Berg, 2001; Saito and Moffett, 2001;

76 Saito et al., 2005) and therefore vulnerable to scavenging (Moffett and Ho, 1996). The similar

77 ionic radii and redox potentials of cobalt and manganese (Mn) cause dCo to be actively

78 incorporated into bacterialauthigenic Mn-oxides, which sink from the water column and

79 accumulate in marine sediments (Cowen and Bruland, 1985; Moffett and Ho, 1996; Swanner et

80 al., 2014). Below the euphotic zone, the persistence of labile dissolved cobalt (LCo) throughout

81 the Atlantic indicates that scavenging of dCo, unlike Fe, is slow (Noble et al., 2012). On

82 timescales of ocean circulation, however, scavenging is responsible for decreasing dCo

83 concentrations with depth and for the low ratio between dCo and macronutrients in deep waters

84 relative to phytoplankton biomass (Moore et al., 2013). As these deep waters are repackaged into

85 thermocline water masses and eventually brought to the surface (Sarmiento et al., 2011), the

86 upper ocean would become depleted in cobalt – as well as other hybrid metals like Fe and Mn –

87 without external sources that keep pace with scavenging (Bruland and Lohan, 2003; Noble et al.,

88 2008).

89

90   Yet, the nature of marine cobalt sources is uncertain. In zonal sections of the North and South

91   Atlantic, sources appear to be concentrated along continental margins (Noble and Saito, in prep;

92   Noble et al., 2012). In the western Atlantic, dCo concentrations exceeding 100 pM were

93   associated with the flow of Upper Labrador Seawater, likely gained through intense sediment

94   resuspension along the shelf or input prior to subduction (Noble and Saito, In prep). dCo in fresh

95   and estuarine waters can be 100–1000x greater than seawater (Gaillardet et al., 2003; Knauer et

96   al., 1982; Tovar-Sánchez et al., 2004) and Co is less prone to flocculation in estuaries than other

97   metals (Sholkovitz and Copland, 1982). Terrigenous inputs from the American continent can be

98   clearly seen in lower salinity surface waters influenced by the Gulf Stream (Noble and Saito, in

99   prep; Saito and Moffett, 2002) and Amazon discharge (Dulaquais et al., 2014b). Yet, in both the

100 North and South Atlantic, a much larger dCo plume was associated with the oxygen minimum

101 zones along the Mauritanian and Namibian coasts (Noble and Saito, in prep, Noble et al., 2012).

102 Although these waters are not anoxic, the dCo plumes imply that O_2 over the continental shelf is

103 sufficiently low that reductive dissolution of Mn and Fe oxides in sediments releases a large flux

104 of dCo to the water column (Heggie and Lewis, 1984; Sundby et al., 1986). Drawing from large

105 inventories in the Atlantic OMZs, upwelling along eastern margins provides a large dCo flux to

106 the surface ocean. While surface dCo maxima from atmospheric deposition generally do not

107 appear in vertical profiles, this process may be important for regions that are isolated from

108 continental input or receive very high levels of dust (e.g. the Sargasso Sea, Dulaquais et al.,

109 2014a; Shelley et al., 2012).

110

111 To date, sectional datasets for dCo have been confined to the Atlantic and, as such, our

112 understanding of cobalt cycling may be biased by the dominant processes occurring there. In

113 comparison, the South Pacific receives considerably less dust deposition and river input

114 (Mahowald et al., 2005; Milliman and Farnsworth, 2011), but hosts a much larger and more

115 reducing oxygen minimum zone. Surface transects off Peru and the Costa Rica Dome suggest a

116 large source from upwelling (Ahlgren et al., 2014; Saito et al., 2004, 2005); however, profiles in

117 the tropical Pacific are sparse (Noble et al., 2008; Saito et al., 2014). We measured the

118 concentration of dissolved cobalt and labile dissolved cobalt concentrations from in over 750

119 samples collected onboard the 2013 US GEOTRACES GP16 expedition across the South Pacific

120 along 12° S, intersecting coastal upwelling along the Peru margin, hydrothermal venting over the

121 East Pacific Rrise, and oligotrophic conditions near Polynesia (Fig. 1). Across this section, the

122 distribution of dCo and LCo follow the intensity of the oxygen minimum zone, with highest

123 concentrations near the South American shelf and low concentrations in both deep waters and

124 oligotrophic surface waters, matching OMZ-associated plumes observed in the Atlantic.

125

126 **2. Methods**

127 **2.1 Sample collection and handling**

128 Sampling on GP16 was conducted with a 24--position trace metal clean titanium rosette attached

129 to a non-metallic Kevlar cable designed for the U.S. GEOTRACES program (Cutter and

130 Bruland, 2012). An additional sample was collected from a surface towfish at each station.

131 Subsamples were collected in a Class-100 sampling van from 12 L Go-Flo bottles (General

132 Oceanics) and passed through 0.2 μM Acropack filters (Pall). All bottles were rinsed 3x with

133 sample seawater before being filled entirely, leaving no headspace. For samples analyzed at sea,

134 both dissolved and labile cobalt were analyzed from the same bottle. All samples were kept

135 refrigerated at 4° C until analysis in a HEPA filtered clean van. All of the LCo samples and more

136 than 90 % of dCo samples were analyzed at sea. Samples not analyzed at sea were preserved for

137 dCo immediately after sampling using metal-free gas adsorbing satchels (Mitsubishi Gas

138 Chemical, model RP-3K), using 3–4 satchels per 6 seawater samples. Gas-impermeable plastic

139 bags (Ampac) were heat sealed and were hand carried directly to Woods Hole at 4° C following

140 disembarkation.

141

142 **2.2 Cobalt determination by cathodic stripping voltammetry**

143 dCo and LCo were measured using a cathodic stripping voltammetry (CSV) method optimized

144 for organic speciation by Saito and Moffett, 2001. This method relies on the complexation of

145 inorganic Co species by a strong synthetic ligand, dimethylglyoxime (DMG, $K^{cond} = 10^{11.5\pm0.3}$),

146 which forms a bis-complex, $Co(DMG)_2$, with Co^{2+} that readily absorbs to a hanging mercury

147 drop (Saito and Moffett, 2001). The $Co(DMG)_2$ complex is measured following a fast, 10 V s^{-1}

148 sweep that reduces both the Co-(II) to Co(0) and the DMG to 2,3-bis(hydroxylamino)butane,

149 producing an 8—10 electron decrease in current for each $Co(DMG)_2$ complex (Baxter et al.,

150 1998). The height of the $Co(DMG)_2$ reduction peak at -1.15 V ~~is measured~~ is directly

151 proportional to the Co concentration.

152

153 Triplicate scans of the seawater sample were followed by four standard cobalt additions (25 pM

154 per addition) and the slope of their linear regression (mean $R^2 = 0.998$) was used to calculate the

155 sample specific sensitivity (in nA pM^{-1}). The cobalt concentration was determined by dividing

156 the mean of the three baseline peaks by the sensitivity, and correcting for reagent volume. The

157 average deviation for these triplicate scans was 1.5 pM.

158

159 dCo analyses were conducted after a 1-hour UV oxidation procedure to remove strong organic

160 ligands that prevent DMG from binding Co binding by DMG. UV digestion was performed in 15

161 mL quartz glass tubes using a Metrohm 705 UV digester (Metrohm USA). Temperature was

162 maintained below 20° C to minimize evaporation losses. After UV digestion, 11 mL of sample

163 was pipetted into 15 mL polypropylene tubes and DMG and a buffering agent, EPPS, were

164 added to final concentrations of 400 μM and 3.8 mM, respectively. 8.5 mL of sample solution

165 was added to a Teflon analysis cup and mixed with 1.5 mL of 1.5 M NaNO$_2$, making a final

166 analysis volume of 10 mL.

167

168 LCo was measured after >8 hour incubation of 11 mL of seawater with 400 μM DMG in a

169 Teflon cupvial. LCo is therefore the concentration that will readily exchange with DMG. After

170 this time, the sample was poured into an autosampler-compatible 15 mL poly-propylene tube

171 (separate from those used for dCo analyses) and EPPS was added to 3.8 mM.

172

173 **2.2.1 Preparing reagent and blanks**

174 All bottles and sample tubes were soaked for >1 week in the acidic detergent Citranox, rinsed

175 thoroughly with 18.2 MΩ Milli-Q water (Millipore), filled with 10 % trace metal grade HCl (J.T.

176 Baker) to soak for 10 days, and rinsed thoroughly with ~10 mM TM-grade HCl. DMG (Sigma-

177 Aldrich) was purified by recrystallization in a 1 mM EDTA solution (Sigma-Aldrich). Crystals

178 were filtered, dried, and dissolved in HPLC grade methanol to a concentration of 0.1 M (Saito

179 and Moffett, 2001). EPPS (Fischer) and Sodium Nitrite (Millipore) were both dissolved in 18.2

180 MΩMilli-Q water to 0.5 M and 1.5 M, respectively, and treated with separate batches of

181 thoroughly cleaned Chelex-100 beads (Bio-Rad) to remove background Co and Ni (Price et al.,

182   1989). Standard additions of cobalt were generated by diluting a 1 ppm certified reference

183   standard (SPEX Certiprep) with 10 mM HCl to a concentration of 5.00 nM. 50 μl of this solution

184   was added to the 10mL sample volume for each standard addition (25 pM addition).

185

186   To determine reagent blanks, Co-free seawater was generated by treating UV-seawater with

187   cleaned Chelex-100 beads. The seawater was then UV digested a second time to remove any

188   ligands leached during Chelex treatment. Any dCo measured in the Chelexed seawater derives

189   from addition of Co from analytical reagents. The mean blank for at sea analysis was

190   consistently low: 3.7 ± 1.2 pM (n = 28). For analyses at Woods Hole, mean blank was 4.7 ± 1.4

191   pM (n = 12). Blanks were subtracted from all measured values. Detection limits were calculated

192   as triple the standard deviation of the blank: 3.6 pM for at-sea analyses and 4.2 pM for samples

193   measured in Woods Hole.

194

195   **2.2.2 Automated cobalt analyses**

196   To accommodate a greater number of samples, our previous workflow (Noble et al., 2008) was

197   modified to incorporate fully automated sample analyses using the Metrohm 85837 Sample

198   Processor autosampler. All measurements were performed using an Eco-Chemie μAutolabIII

199   system connected to a Metrohm 663 VA stand. A hanging drop mercury electrode (Metrohm)

200   was set to semi-hanging drop mode and accompanied by a 3 M KCl/AgCl reference electrode

201   and glassy carbon auxiliary electrode. Scheduling and data acquisition were controlled using

202   NOVA 1.8 software (Metrohm Autolab B.V). Automated delivery of seawater, sodium nitrite,

203   and Co standard to the analysis cup was accomplished by three dedicated Dosino 800 burettes

204   (Metrohm). Sample volume was increased to allow ~2 mL for conditioning tubing and analysis

205   cup prior of sample delivery.

206

207   Tubes containing 11 mL seawater, DMG, and EPPS were inverted several times and placed onto

208   a sampling rack where 8.5 mL of the mixture was dosed into the Teflon analysis cup. 1.5 mL of

209   1.5 M sodium nitrite was added directly to the sample cup. Samples were purged with high-

210   purity N_2 (>99.99 %) for 180 s and then conditioned for 90 s at -0.6 V. Scan sweeps were run at

211   10 V s^{-1} from -0.6 V to -1.4 V. Before each analysis, the sample cup was rinsed fully with Milli-

212   Q water and 1 mL sample before measurement. Between uses, autosampler tubes, quartz vials,

213   and Teflon cups were rinsed with 10 mM HCl, 18.2 MΩ water~~Milli-Q water~~, and 1-2 mL of new

214   sample. The autosampler ~~sample~~ uptake line was rinsed with 10 mM HCl and 18.2 MΩ water

215   ~~Milli-Q~~ when transitioning from LCo analyses to dCo analyses.

216

217   We noticed a decrease in sensitivity of preserved samples relative to those analyzed at sea,

218   possibly caused by an increase in the sample pH during storage. Sensitivity was restored by

219   doubling the concentration of our buffering agent, EPPS, in the sample to a final concentration of

220   7.6 mM. We tested a broad~~er~~ range of EPPS additions in UV seawater and found the cobalt

221   concentration unchanged while the ~~deviation~~ variance between triplicate scans was reduced

222   markedly by the increase in sensitivity (data not shown). We tentatively attribute this decrease in

223   sensitivity in preserved samples to CO_2 adsorption by gas satchels, which would increase sample

224   pH.

225

226   **2.2.3 Signal processing**

227 Analyses conducted at sea were characterized with a mild to moderate electrical interference that

228 mandated additional processing before peak height could be reliably measured (Fig. 2). We

229 opted for a simplified least squared fitting routine included in the NOVA software package that

230 conducts a 15-point weighted moving average – equivalent to a 36.9 mV ~~analytical~~ window –

231 according to a 2nd order polynomial. This method did not distort measured peak height ~~cobalt~~

232 ~~concentrations~~ when noise was low (Fig. 2a, b). A small fraction of scans (~3 %) were not

233 adequately fit using this routine and were instead smoothed using a 9-point linear moving

234 average (22.1 mV window, Fig. 2c), also included in NOVA. For all samples, peak height was

235 measured manually to minimize peak distortion due to added noise.

236

237 Subsequent analyses in the laboratory at Woods Hole were able to remove this signal by

238 increasing the current sampling step from 2.46 mV (341 points between -0.6V to -1.4V) to 4.88

239 mV (174 points) which eliminated the need for smoothing prior to sample analysis. We observed

240 good agreement between samples analyzed at sea and in the lab, indicating that the smoothing

241 procedures applied at sea did not bias the data and that gas adsorbing satchels preserved original

242 concentrations (Noble and Saito, in prep).

243

244 2.2.4 Intercalibration and internal laboratory standard

245 All data reported in this manuscript have been submitted to the Biological and Chemical

246 Oceanography Data Management Center (BCO-DMO, http://www.bco-

247 dmo.org/dataset/647250). Our laboratory continues to participate in international intercalibration

248 efforts through the GEOTRACES program in anticipation of the release of the 2nd Intermediate

249 Data Product, Summer 2017. The sampling scheme for GP16 included 2 overlapping samples

250   per full depth profile where the shallowest sample of the deep cast matched the deepest sample

251   for the mid cast, and the shallowest sample from the mid cast matched the deepest sample from

252   the shallow cast (i.e. a 36-point profile is composed of 34 discreet depths and 2 overlapping

253   depths). Comparing overlapping samples collected at the same depth and location on separate

254   hydrocasts provides a measure of reproducibility. The average difference between dCo analyses

255   across 40 overlapping depth samples was 5.7 pM with a median difference of 3.5 pM. For labile

256   cobalt, average deviation was 2.1 pM (median of 2.0 pM, n = 41). Least-squares regression of

257   these samples yielded slopes close to 1(0.98 for dCo and 0.96 for LCo; y-intercept forced to 0),

258   indicating good reproducability. Furthermore, comparisons with other groups measuring dCo in

259   the same samples reported here suggest strong agreement between groups despite major

260   methodological differences (C. Parker and K. Bruland, personal communication).

261

262   Because acidified community reference materials such as the SAFe standards require a delicate

263   neutralization to pH 7.5–8 prior to analysis, a large batch of UV oligotrophic seawater was

264   generated prior to the cruise and used to assess instrument performance during at-sea analysis.

265   This consistency seawater standard was run ~3x per week, as were blanks, and values were

266   stable over several reagent batches for the duration of the cruise (4.5 ± 2.1 pM, n = 28). SAFe

267   standard D1 was measured at sea (48.5 ± 2.4 pM, n = 3) and fell within 1 SD of the consensus

268   value (46.6 ± 4.8 pM). SAFe standard D2 and GEOTRACES standard GSP were run at higher

269   frequency for analyses at Woods Hole. Our measurements of D2 (46.9 ± 3.0 pM, n = 7) agreed

270   with consensus values (45.7 ± 2.9 pM) and concentrations from our lab published previously

271   (Noble et al., 2012). While the GSP standard does not have a consensus value, our

272   determinations (2.5 ± 2.0 pM, n = 10) are within the range for SAFe S (4.9 ± 1.2 pM), which was

12

273 collected at the same offshore location as GSP. Acidified SAFe and GEOTRACES standards

274 were neutralized with concentrated ammonium hydroxide (Seastar), mixing the entire sample

275 between drops, prior to UV digestion. When base was added more quickly, measured dCo was

276 halved, presumably due to adsorption or co-precipitation onto magnesium hydroxides formed

277 during base addition. For analysis of neutralized standards, we found a ~6:1 EPPS:NH$_4$OH

278 (M:M) buffer improved pH stability during analysis and removed significant baseline drift

279 observed with samples solely buffered with EPPS.

280

281 **2.3 Particulate metal analyses**

282 Particulate material collected from Go-Flo bottles was filtered onto acid-cleaned 0.45 μm

283 polyethersulfone filters (25 mm). Digestion protocol and analyses are identical to those used to

284 measure particulate metal concentrations during the North Atlantic GA03 cruise, described in

285 Twining et al., 2015. After filtration, filters were halved, digested at 135° C in sealed Teflon

286 vials containing 4 M HCL, 4 M HNO$_3$, and 4 M HF;, digests were then dried, and re-dissolved in

287 0.32 M HNO$_3$ before analysis. pCo, pMn and pP concentrations were measured by ICP-MS

288 (Element 2, Thermo Scientific), calibrated using external multi-element standard curves, and

289 corrected for instrument drift and sample recovery by In and Cs internal standards. More detailed

290 methods for this dataset can be found elsewhere (Ohnemus et al., In ReviewPress).

Field Code Changed

291

292 **3. Results**

293

294 We report 680 determinations of dissolved cobalt (dCo) and 783 determinations of labile

295 dissolved cobalt (LCo) measured at sea, onboard the GP16 expedition in October–December

12

296   2013, as well as an additional 140 measurements of dCo measured from preserved samples on

297   land. In this section, we describe the distributions of dCo, particulate cobalt (pCo), and LCo in

298   the South Pacific Ocean.

299

300   **3.1 Dissolved Cobalt**

301   Throughout the GP16 transect, nutrient uptake and scavenging result in a hybrid-type profile for

302   dCo dissolved cobalt (dCo, Fig. 3), similar to dCo profiles from the Atlantic (Bown et al., 2011;

303   Dulaquais et al., 2014b; Noble et al., 2012; Noble and Saito, in prep) and North Pacific (Ahlgren

304   et al., 2014; Knauer et al., 1982; Saito et al., 2014). dCo ranged from <3 pM (below detection) in

305   the South Pacific Gyre (e.g. Stations 23, 36) to 210 pM beneath the oxycline near the Peru

306   Margin (Station 1). In the deep Pacific, concentrations fell between 20–40 pM but increased

307   slightly at deepest stations below 4500 m. These values are much less than those observed in

308   zonal transects surveying the North and South Atlantic (Noble et al., 2012; Noble and Saito, in

309   prep) but are similar to measurements in the Southern Ocean (Bown et al., 2011), indicating that

310   dCo is scavenged in the deep ocean along meridional overturning circulation. Below 3000 m,

311   dCo is somewhat lower east of the Eastern Pacific Rise (EPR), and matches less oxygenated,

312   older waters than in the western portion of the transect (Fig. 4). While many profiles west of the

313   EPR show considerable variation between 2000–3000 m suggestive of hydrothermal influence,

314   the range is small (<10 pM) relative to background concentrations (30–40 pM) and unlike the

315   50-fold excess of hydrothermal dFe and dMn above background seawater measured at Station 18

316   (Resing et al., 2015).

317

318   dCo peaks in the mesopelagic, typically between 300–500 m. Towards the Peru shelf, this

319   maximum shoals and increases, following the position and intensity of the oxygen minimum

320   zone (OMZ, defined here as ~~O_2~~ <~~-~~20 μM O_2). Although the OMZ is several hundred meters thick

321   near the eastern margin (Fig. 3), dCo concentrations >100 pM are restricted to samples collected

322   just below the oxycline. Despite this narrow depth range, ~~dCo~~ >100 pM <u>dCo</u> extends as far as

323   100° W. For all depths below 200 m, dCo follows a negative linear relationship with O_2 (Fig.

324   5a). Over the Peru shelf, maximum dCo was measured at the top of the OMZ and dCo decreased

325   with depth (except for the shallowest and most shoreward Station 2). Only at the western edge of

326   the section do dCo and O_2 decouple: the dCo maximum at <u>S</u>~~s~~tation 36 is deeper (500–1000 m)

327   than the oxygen minimum (300–500 m), seemingly independent of the influence of the South

328   Pacific OMZ (Fig. 3).

329

330   All profiles show a surface or near-surface minimum that indicates biological uptake and export.

331   As a result, dCo is well traced by dissolved phosphate, PO_4, in the upper 200 m of the ETSP

332   (Fig. 5c). This relationship holds despite sharp transitions to high dCo in the oxycline near the

333   Peru shelf. Upwelling of O_2-depleted, PO_4-rich waters <u></u>~~along the eastern boundary results~~

334   <u>contributes to high dCo in the surface ocean along the eastern margin</u>~~in high surface dCo,~~ <u>with</u>

335   <u>concentrations</u> decreasing westward due to mixing and export. A secondary surface dCo

336   maximum marked a cyclonic eddy sampled at 89° W (Station 9, V. Sanial, personal

337   communication), which appeared to transport a shelf-like dCo and LCo signature for the upper

338   300 m into the offshore OMZ (Fig<u>s</u>. 6<u>a, b</u>). ~~Toward~~ <u>In</u> the South Pacific gyre, dCo in the

339   euphotic zone falls below 10 pM. While the lowest PO_4 was found in low salinity surface waters

340   west of 140° W, minimum dCo and deepest nutriclines corresponded to a southwestward

341 excursion in the transect between Stations 17–23 (109–120° W), which were accompanied by

342 high salinities (>36) associated with the eastern part of the subtropical gyre (Fig. 13). In contrast

343 to the deep, smooth dCo nutricline further to the east, stations at the western edge of the section

344 (Stations 32, 34, and 36) contained 20 pM Co until ~50 m where concentrations decrease sharply

345 surfaceward, resembling profiles in the North Atlantic (Fig. 3; Noble and Saito, in prep).

346

347 **3.2 Particulate Cobalt**

348 The surface minimum in dCo is mirrored by a near-surface maximum in particulate cobalt (pCo)

349 from biological uptake throughout the GP16 section. The distribution of pCo (Fig. 6c) resembles

350 particulate phosphorus (pP), chlorophyll, and other indicators of phytoplankton biomass. Very

351 high pCo (>10 pM) was measured in the highly productive waters in the Peru upwelling

352 ecosystem while lower concentrations (2–4 pM) were found in oligotrophic surface waters. West

353 of 100° W on the GP16 transect, a secondary pCo maximum between 300–500 m overlaps with

354 high particulate Mn (pMn), reflecting Co incorporation into Mn-oxides in oxygenated

355 thermocline waters (Fig. 6c). Elevated pCo was also found at the top of the OMZ in the eastern

356 half of the transect, corresponding with high dCo from remineralization. High pP and low pMn

357 in these samples suggest that pCo may be present as biomass in anoxic bacterial and archaeal

358 communities (Ohnemus et al., In ReviewPress), rather than incorporation into bacterial Mn-

359 oxides by co-oxidation. pMn increases sharply west of 100° W, implying that pCo here is present

360 as an authigenic phase (Fig. 9, Ohnemus et al., In ReviewPress; Moffett and Ho, 1996).

361

362 **3.3 Labile Dissolved Cobalt**

363 dCo can be bound by extremely strong organic ligands that affect its reactivity (Ellwood and van

364 den Berg, 2001; Saito and Moffett, 2001). These ligands may be composed of degradation

365 products of the cobalt-bearing cofactor vitamin B_{12} and may be stabilized following oxidation of

366 Co(II) to Co(III) (Baars and Croot, 20145). Unlike other metals such as Fe, dCo bound to natural

367 ligands is kinetically inert to ligand exchange (although some forms may still be bioavailable)

368 and strong Co(II) ligands are not in excess of dCo, largely due to binding competition with

369 nanomolar levels of labile nickel (Saito and Moffett, 2001; Saito et al., 2005). These properties

370 can result in a significant fraction of labile dissolved cobalt (LCo) that can be measured without

371 the UV-oxidation procedure necessary to measure dCo, especially in the mesopelagic (Noble et

372 al., 2012).

373

374 On GP16, the distribution of LCo is similar to that of dCo (Figs. 3, 4, 6). Except for samples

375 from the upper 50 m, dCo and LCo form a linear relationship ($R^2 = 0.88$) whose slope indicates

376 that ~33 % of dCo is labile (Fig. 7a). Major exceptions are confined to the highly productive

377 waters over the Peru shelf (Stations 1–6) where LCo is much lower than expected from dCo. In

378 these waters, LCo decreases in step with silicate (Fig. 7c). As in the North and South Atlantic

379 (Noble et al., 2012; Noble and Saito, in prep), LCo is undetectable in the surface ocean outside

380 of the waters influenced by upwelling (beyond 100° W, Fig. 6b). The absence of LCo from the

381 upper 300 m of the water column is deeper than corresponding gradients in the Atlantic,

382 suggesting cobalt depletion is more intense in the South Pacific.

383

384 In the deep Pacific (>3000 m), where dCo is low, LCo is undetectable. LCo remains low (<15

385 pM) in the mesopelagic, except where the OMZ is most intense (Fig. 4). Within the OMZ, LCo

386 maxima coincide with dCo maxima (Stations 1–15), but further to the west these LCo maxima

387 are much less ~~intense~~ pronounced and occur deeper than dCo maxima (Fig. 3). The LCo plume

388 from the OMZ also extends deeper (below 2000 m) than the corresponding dCo (<2000 m),

389 suggesting that remineralization and scavenging affect these quantities in different ways. Slight

390 secondary maxima between 1500–2000 m (10–15 pM) appear in the center of the section on $\sigma_\theta =$

391 27.7–8 kg m^{-3} isopycnal layers (Fig. 4c, 105° W–115° W), perhaps tracing transport of LCo

392 remineralized in the eastern basin as these waters flow over the mid ocean ridge.

393

394 **4. Discussion**

395

396 ~~4.1 Basin-scale coupling between dCo and O$_2$~~

397 The most striking aspect of the dCo distribution in the ETSP is the very high concentrations

398 present in the OMZ (Figs. 3–5). Similar distributions have been observed in both the North and

399 South Atlantic, where >100 pM dCo plumes corresponded to low oxygen waters underneath the

400 Benguela and Mauritanian upwelling systems (Noble et al., 2012; Noble and Saito, in prep). In

401 the North Pacific, profiles from the Costa Rica Dome (Ahlgren et al., 2014), the California

402 margin (Biller and Bruland, 2013; Knauer et al., 1982), and the Central Pacific along 155° W

403 (Saito et al., 2014) support an OMZ-cobalt plume there as well. Based on measurements from

404 these four OMZs, oxygen biogeochemistry seems to exert a major control on cobalt cycling

405 throughout the oceans. It is interesting to note that the magnitude of the observed dCo plumes

406 does not appear to scale with minimum O$_2$ between Atlantic and Pacific OMZs. While minimum

407 O$_2$ in the Atlantic OMZs exceeds 20 μM, much of the ETSP is anoxic (Karstensen et al., 2008;

408 Ulloa et al., 2012). Yet, dCo in the ETSP occupies a similar 100–200 pM range reported for the

409 North and South Atlantic OMZs (Noble et al., 2012; Noble and Saito, in prep). Clearly, other

410 factors besides O_2 alone contribute to large scale plumes of dissolved cobalt in the oceans.

411

412 In the following, we describe the oceanographic processes that lead to elevated dCo and LCo

413 concentrations in low-oxygen waters (Section 4.1). At the basin scale, the combined effects of

414 remineralization and circulation link dCo with O_2 throughout the water column in the ETSP

415 (Section 4.1.1). The 'cobalt plume' in the OMZ, however, is more than an extrapolation of these

416 mechanisms, requiring a large coastal source (Section 4.1.2), and suppression of dCo scavenging

417 at very low O_2 (Section 4.1.3). The mechanism, magnitude, and redox sensitivity of the coastal

418 Co source are then examined in greater detail (Section 4.2). Finally, we highlight the scarcity of

419 dCo – a critical micronutrient to phytoplankton – in the surface ocean of the South Pacific and

420 the dependence of surface ocean dCo supply on coastal sources (Section 4.3).

421

422

423 Between the Atlantic and Pacific basins, the magnitude of the observed dCo plumes does not

424 appear to scale with minimum O_2. While offshore O_2 in the Atlantic OMZs exceeds 20 μM,

425 much of the ETSP is anoxic (Karstensen et al., 2008; Ulloa et al., 2012): Winkler titrations of

426 discreet samples measured on the GP16 cruise indicate minimum O_2 to be <5 μM, while *in situ*

427 sensors suggest true concentrations in the ETSP can be even lower (Thamdrup et al., 2012). Yet,

428 dCo in the ETSP occupies a similar 100–200 pM range reported for the North and South Atlantic

429 OMZs (Noble et al., 2012; Noble and Saito, in prep). Either the redox thresholds that affect

430 processes like water column scavenging or sedimentary release are met in the suboxic Atlantic as

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~~well as the anoxic Pacific, or the apparent evenness in dCo concentration between OMZs results~~

~~from other factors besides O$_2$ (e.g. continental sources, dust, remineralization).~~

4.1. Processes generating the OMZ cobalt plume in the Eastern South Pacific Ocean

4.1.1 Basin-scale remineralization and circulation couple dCo with O$_2$

In the ETSP, tight coupling between dCo and O$_2$ is evident in the ~~results in the~~ strong, inverse

relationship that describes all samples below 200 m (Fig. 5a). In light of the nutrient-like dCo

depletion in the surface of the ETSP and elsewhere (Fig. 6, Ahlgren et al., 2014; Dulaquais et al.,

2014b; Noble et al., 2012), this negative correlation might be attributed to remineralization: dCo

is returned to the dissolved phase from a sinking biogenic phase following respiration (i.e. O$_2$

consumption). The slope of the dCo:O$_2$ line (-0.33 μM M^{-1}, R^2 = 0.75 for 200–5500 m) ~~might~~

would then represent the biological stoichiometry of the exported organic material in the ETSP.

However, Co:P ratios in particulate material collected in the upper 50 m on GP16 indicate

greater phytoplankton cobalt utilization (median pCo:pP of 140 μM M^{-1} ÷ 118 O$_2$:P M M^{-1} = 1.2

Co:O$_2$ μM M^{-1}; ~~Fig. 13C;~~ DeVries and Deutsch, 2014). If the dCo:O$_2$ trend is borne solely from

remineralization, a greater slope would be expected, implying removal of dCo by scavenging.

The linearity in the dCo:O$_2$ relationship is also not reproduced upon conversion of O$_2$ to apparent

oxygen utilization (AOU = O$_{2,saturation}$ − O$_{2, measured}$, Fig. 5b, R^2 = 0.49), ~~implying~~ further

suggesting that other factors besides remineralization (such as circulation and scavenging) shape

the subsurface dCo distribution as well.

In the deep ocean, near-conservative mixing of ~~dCo with high and~~ low O$_2$-/high dCo water

masses with high O$_2$/low dCo water masses probably contributes to the observed dCo:O$_2$

454 relationship. The enormous depth range (>5000 m) described by the linear $dCo:O_2$ relationship

455 contrasts with the near-exponential decrease in remineralization rates with depth (e.g. Karstensen

456 et al., 2008). It is likely that deep Pacific circulation acts to spread signals of local dCo

457 remineralization throughout the water column, aggregating a multitude of export stoichiometries

458 and remineralization processes into a single, coherent relationship across the basin. LCo is

459 undetectable below ~2500 m and the shallower slope of the $LCo:O_2$ trend (-0.11 $\mu M\ M^{-1}$, $R^2 =$

460 0.67, not shown) implies that the $dCo:O_2$ relationship is driven mostly by strongly complexed

461 species, which are less vulnerable to co-oxidation by Mn-oxidizing bacteria in the water column

462 (Moffett and Ho, 1996). Since the deep Pacific can be broadly regarded as a mixture of

463 oxygenated circumpolar waters and OMZs (especially from the North Pacific), the linear $dCo:O_2$

464 relationship between 200 and 5500 m may reflect mixing of a dCo pool that is largely inert to

465 losses by scavenging.

466

467 In the upper 200 m, dCo is not well coupled with O_2 and almost all samples fall above the line

468 established by deeper samples (Fig. 5a). Near the South American margin, the dCo maximum in

469 the upper OMZ is more than ~~double~~ twice the dCo concentration expected by extrapolation of

470 the basin-scale $dCo:O_2$ relationship to the 0 μM O_2 intercept ~~of the dCo:O₂ relationship from~~

471 ~~deeper waters~~ (77 pM, Fig. 5a). ~~Given their resemblance~~The similarity of dCo profiles to

472 profiles of excess N_2 from denitrification from this region (e.g. Chang et al., 2010)~~(Chang et al.,~~

473 ~~2010),~~ implies that ~~it is likely that~~ both the dCo maximum in the OMZ and its decrease with

474 depth are driven by factors that also affect nitrogen loss: namely~~a combination of~~ in-situ

475 remineralization of sinking biogenic particles ~~cobalt~~ and lateral transport of coastal waters that

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476　experience high rates of denitrification and are also rich in dCo ~~of a coastal cobalt source~~

477　(DeVries et al., 2012).

478

479　**4.1.2 Distinct surface and mesopelagic Co:P relationships**

480　In the upper ocean (0–200 m), dCo is linearly related to PO_4 (Figs. 5c ~~and 7b~~), indicating that the

481　processes controlling PO_4 in the surface – upwelling, mixing, biological uptake and export – are

482　the main drivers of dCo as well. In the upper 50 m, the dCo:PO_4 slope (69 μM:M, R^2 = 0.89, Fig.

483　7b) may describe export stoichiometry throughout the Eastern Pacific. That the surface dCo:PO_4

484　slope intercepts the highest dCo concentrations (below the 50 m depth range of the regression,

485　Fig. 5c, cyan line) indicates that new cobalt sourced from the shelf is rapidly incorporated into

486　~~biological~~ the biological cycl~~ing~~ and that the capacity for phytoplankton Co uptake is not

487　overwhelmed by the order of magnitude higher dCo in coastal waters relative to the open ocean.

488　Culture experiments with model diatoms and coccolithophores demonstrate this capacity

489　(Shaked et al., 2006; Sunda and Huntsman, 1995; Yee and Morel, 1996), deploying Co to zinc

490　enzymes to maintain activity when Zn becomes scarce. When Zn is limiting, Co quotas, as

491　~~judged by~~observed in open ocean phytoplankton ~~(Sunda and Huntsman, 1992; Twining and~~

492　~~Baines, 2013)~~, are 10–100x greater than Co quotas when Zn is replete (Sunda and Huntsman,

493　1992; Twining and Baines, 2013). Therefore, minor substitution of Zn quotas by Co (~10 %) can

494　double cellular Co levels in eukaryotes, resulting in nearly complete uptake of dCo from the

495　surface ocean.

496

497　A separate nutrient-like dCo:PO_4 trend arises from gradients of both elements in the open ocean

498　nutricline (Fig. 5c). The slope of the mesopelagic trend (16 μM:M, for 200–1000 m, red line in

499 Fig.~~ure~~ 5c) is much less than that measured for the upper 50 m (69 µM:M, cyan line). Due to

500 considerable preformed PO_4 in deep waters, as well as elevated $dCo:PO_4$ ratios in the OMZ, the

501 mesopelagic $dCo:PO_4$ regression is ~~considerably~~ less robust than in the surface ($R^2 = 0.21$),

502 though the slope does reflect dCo and PO_4 covariation in this depth range when PO_4 is <-2 µM

503 (Fig. 5c, red line). Regardless, there seems to be a fundamental mismatch between $dCo:PO_4$ from

504 the upper water column (0–200 m) and that observed deeper (200–1000 m).

505

506 -In the eastern margin, the surface and mesopelagic $dCo:PO_4$ vectors are joined at 2.6 µM PO_4

507 by a near-vertical line that makes the $dCo:PO_4$ domain triangular. Interpretation of this line

508 depends largely on its perceived direction: a downward vector can be a fingerprint of scavenging

509 while an upward vector describes a cobalt source (Noble et al., 2008; Saito et al., 2010). This

510 ambiguity is clarified by examining $dCo:PO_4$ gradients within isopycnal surfaces, which strongly

511 indicate a source at low O_2. In the ETSP, σ_θ 26.2 and 26.4 isopycnals host the upper OMZ and

512 the oxygenated thermocline waters west of 100° W. Water masses on these surfaces can be

513 distinguished on the basis of salinity; from the GP16 dataset, mixing between salty and

514 deoxygenated equatorial sub-surface waters (ESSW or 13° C water) with fresher, ventilated Sub-

515 Antarctic waters is apparent (Fiedler and Talley, 2006; Toggweiler et al., 1991). Oxygenated

516 waters on $\sigma_\theta = 26.2$ and 26.4 show a tight coupling between dCo and PO_4 from remineralization

517 of both elements (Fig. 8a). For samples with <-20 µM O_2, however, deviation from the oxic

518 $dCo:PO_4$ trend is always positive, indicating a dCo source within the OMZ. When oxygen is

519 low, dCo follows salinity (Fig. 8b). Mixing of high salinity (34.9–35.0), high dCo ESSW from

520 the northeast with low salinity, low dCo Subantarctic waters explains the dCo:salinity

521 covariation on these isopycnal surfaces. While ESSW is fed by the ~~lower~~ equatorial undercurrent

522 (EUC), which originates near Papua New Guinea and transports a large Fe and Al source

523 eastward (Slemons et al., 2010), it is low in dCo (as measured at 155° W, Hawco and Saito,

524 unpublished; Saito et al., 2014). When the EUC bifurcates near the Galapagos, it mixes with

525 coastal waters north and south of the equator (Fiedler and Talley, 2006; Stramma et al., 2010),

526 where its high dCo signature is likely acquired.

527

528 **4.1.3 Suppression of cobalt scavenging in the OMZ**

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529 The isopycnal dCo:salinity relationship ~~also~~ implies cobalt scavenging in the OMZ is low (Fig.

530 8b). This is not surprising given the slower rates of ~~thermodynamic~~ ~~barriers to~~ MnO_2 formation

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531 at low O_2 (Johnson et al., 1996; von Langen et al., 1997) and very low particulate Mn measured

532 in the ETSP OMZ (Ohnemus et al. In Press~~Fig. 9~~). In the OMZ, both pCo:pP and pMn:pP ratios

533 in the OMZ are consistent with micronutrient use by microbial communities and resemble

534 biomass collected in the euphotic zone on GP16 (Co:P = 0.5–4 x 10^{-4} M M^{-1}, Mn:P ~10^{-3} M M^{-1},

535 ~~Ohnemus et al., In Review~~; Fig. 9, pink and cyan lines). These low, biomass-like pCo:pP and

536 pMn:pP signatures in the ETSP OMZ are consistent with thermodynamic and kinetic ~~redox~~

537 barriers to Mn oxidation at very low O_2 (Ohnemus et al., In Review).

538

539 Crossing the anoxic/oxic transition at 100° W in the thermocline (σ_θ 26.2–27.0, centered at 300

540 m) results in a factor of ten higher pMn concentrations and implies a redox threshold to Mn

541 oxidation in the mesopelagic (Fig. 9, blue circles). Heterotrophic Mn-oxidizing bacteria are

542 known to incorporate Co by enzymatic co-oxidation into the Mn-oxide lattice and are prevalent

543 throughout the water column (Cowen and Bruland, 1985; Moffett and Ho, 1996). While

544 particulate Co profiles in the ETSP have a near-surface maximum from biological uptake (Fig.

545   67c), pCo attenuates much less with depth than pP in oxic thermocline waters. Very high pCo:pP

546   ratios (up to 10^{-3} M M^{-1}) are found in the oxygenated thermocline but not in the OMZ (~~σ_θ 26.2~~

547   ~~27.0,~~ Fig. 9, pink circles). The coincidence of high pCo:pP and high pMn throughout the ~~in the~~

548   mesopelagic is consistent with pCo being present in an authigenic Mn-oxide phase, marking an

549   important transition between nutrient-like cobalt cycling in the surface ocean (where pCo is

550   almost entirely biogenic) to Mn-oxide driven scavenging at depth.

551

552   The stimulation of cobalt scavenging across the anoxic/oxic transition at 100° W was also

553   reflected in a sharp decrease in LCo:PO$_4$ as scavenging removed LCo from the water column

554   (Fig. 9, black circles). Indeed, the same oxygenated thermocline samples with high pMn and

555   pCo:pP are responsible for the ~~shallow vector~~ gradual slope in dCo:PO$_4$ space (16 μM M^{-1}, Fig.

556   5c, red line). The offset between high surface and low mesopelagic dCo:PO$_4$ is mirrored by the

557   lower surface and higher mesopelagic pCo:pP. While scavenging is often presumed to draw

558   chiefly from metals in the dissolved phase, the heterotrophic nature of Mn-oxidizing bacteria and

559   their abundance in sediment traps hint that Mn-oxidizing bacteria may access biogenic metal

560   pools within sinking particles (Cowen and Bruland, 1985). In such a case, pCo may be shunted

561   directly from a biogenic to an authigenic phase without being truly remineralized, preventing the

562   equal return of dCo at depth relative to that exported from the surface, as documented here by the

563   disparity between deep and shallow dCo:PO$_4$ slopes (Fig. 5c)~~14)~~. An important consequence of

564   mesopelagic scavenging is that ventilation of these waters by upwelling without an exogenous

565   source (e.g. the continental margin~~margin sediments~~) would create conditions whereby dCo,

566   relative to PO$_4$, is not supplied to the same extent it is presently utilized and exported. Because

567   these scavenged waters are relatively shallow and have short ventilation ages (Fiedler and Talley,

2006), fluxes of cobalt to the South Pacific from margin sources must be ~~sufficiently rapid~~large enough to balance these scavenging losses.

4.3 4.2 A major cobalt source from the Peruvian ~~shelf~~margin

4.2.1 Water column signatures of a dCo source

The strong covariation between high dCo and low O_2 in the ETSP and the intersection of the OMZ with the South American margin suggests that ~~reducing sediments along~~ the continental shelf may be an important cobalt source. Sections from the North and South Atlantic (Noble et al., 2012; Noble and Saito, in prep) and profiles from the North Pacific (Ahlgren et al., 2014; Knauer et al., 1982) have resulted in similar assertions, but the coincidence of high phytoplankton productivity along eastern margins also imprints signals from elevated remineralization. This is certainly the case for the ETSP, where ~~S~~stations 2 and 3 on the Peru shelf featured >~1.5 μg chlorophyll L^{-1} in the euphotic layer, and >~4 μM nitrite throughout the OMZ from intensified anoxic remineralization. As a result, the dCo profile in Peru shelf waters strongly resembles PO_4 and other nutrients above the oxycline (Fig. 10). Unlike PO_4, however, these shelf stations show a dCo maximum at the oxycline and decreasing concentrations with depth that more strongly resembles the Mn profile (Fig. 10), implying that additional process contribute to the dCo profile over the shelf. ~~As a result, all but one station along the shelf shows a dCo maximum at the oxycline, rather than the benthic boundary layer (Fig. 10). The lone exception, Station 2, is also the most shoreward, having respective dCo and LCo maxima of 159 pM and 59 pM at the deepest depth (110 m), indicating a flux of cobalt to the water column.~~

590 Positive correlations between dCo, LCo and dMn within the OMZ on the Peru shelf reflect a

591 shared source (Fig. 11). The slope of the LCo:dMn relationship (18 ± 2 mM M^{-1} R^2 = 0.76) is

592 nearly identical to that in upper continental crust and Andesite (21–26 mM M^{-1}, McLennan,

593 2001; Taylor and McLennan, 1995), matching expectations that mineral dissolution should

594 provide labile Co. However, the steeper slope for the dCo:dMn relationship (42 ± 5 mM M^{-1} R^2

595 = 0.67) exceeds crustal endmembers. Addition of a second, Co-enriched component is needed to

596 explain the observed relationship. Given the massive productivity over the Peru shelf, biological

597 export and remineralization of dCo and dMn in the OMZ is a reasonable cause for the high

598 Co:Mn ratio in the shelf OMZ. From particulate material in the upper 40 m of shelf stations (1–

599 5), the average Co:Mn ratio in local biomass is between 100 and 110 mM M^{-1} (median and

600 mean), roughly 5 times higher than continental crust, and falling within the range reported for

601 single cell analysis of phytoplankton cells from other regions (70–400 mM M^{-1}, Twining and

602 Baines, 2013). The combination, then, of a high biotic Co:Mn and a lower ratio from a

603 sedimentary source can produce the slope observed in the water column, but requires

604 remineralized dCo to be chiefly ligand-bound in order to preserve the near-crustal LCo:Mn

605 slope. The higher Co:Mn ratio in biomass relative to their shared sedimentary source also results

606 in a nutrient trap that returns upwelled dCo to the OMZ more efficiently than dMn and implies

607 that input of dCo from the shelf is rapidly followed by biological utilization, evident in the

608 immediate transition from a dMn-like profile below the oxycline to a PO$_4$-like profile above it

609 (Fig. 10).

610

611

612 Water column observations of a large dCo source are also mirrored in the depleted Co contents

613 of continental shelf sediments along the Peru margin. A survey of continental shelf sediments

614 underlying the Peru OMZ found low Co/Al ratios (1.2 ± 0.3 x 10^{-4} g g^{-1}, Böning et al., 2004)

615 relative to Andesitic and upper continental crusts (2.63 and 2.11 x 10^{-4} g g^{-1} respectively,

616 McLennan, 2001; Taylor and McLennan, 1995), requiring that about half of the Co delivered to

617 the continental shelf from crustal sources dissolved prior to long-term burial on the shelf. The

618 only other element to have a similar depletion was Mn, which covaried with Co across all

619 samples in the Böning et al. study, consistent with release of both metals by reductive

620 dissolution. Yet the exact mechanism for dCo release is unclear: mass balance calculations for

621 Mn indicate that diffusive fluxes from sediment porewaters on the Peru Shelf are much too slow

622 to account for solid-phase Mn/Al deficits that accumulate in the sediment column (Scholz et al.

623 2011). Therefore, most Mn is released prior to sedimentation on the margin, either by dissolving

624 directly in the water column or through upstream release in estuaries. Since Co covaries with Mn

625 in both dissolved and sediment phases (Fig. 11, Böning et al., 2004), the ultimate source of the

626 dCo plume in the Peruvian OMZ may not be generated by diffusion from margin sediments

627 either. Near-surface Co and Mn content were slightly higher in the shallowest sediments (<150

628 m water column depth) and uniformly low at deeper locations (Böning et al., 2004), implying

629 that sedimentation outpaces dissolution of Co and Mn only in very shallow water columns and/or

630 proximal to input, which explains the lack of dissolved benthic maxima for both elements

631 beyond Station 2 (Fig. 10).

632

633 Positive correlations between dCo, LCo and dMn within the OMZ on the Peru shelf reflect a

634 shared source (Figs. 10, 11). The slope of the LCo:dMn relationship, 18 ± 2 mM M^{-1} R^{2} = 0.76,

635 is nearly identical to that in upper continental crust and Andesite (21–26 mM M^{-1}, McLennan,

636 2001; Taylor and McLennan, 1995), matching expectations that mineral dissolution should

637 provide should provide labile Co. However, the steeper slope for the dCo:dMn relationship (42 ±

638 5 mM M^{-1} R^2 = 0.67) exceeds crustal endmembers. Addition of a second, Co-enriched

639 component is needed to explain the observed relationship. Given the massive productivity over

640 the Peru shelf, biological export of dCo and dMn into the OMZ is a reasonable cause for the high

641 Co:Mn ratio in the shelf OMZ. From particulate material in the upper 40 m of shelf stations (1–

642 5), the Co:Mn ratio in biomass is 100–110 mM M^{-1} (median and mean), ~5 times higher than

643 crust, and falling within the range reported for single cell analysis of phytoplankton cells (70–

644 400 mM M^{-1}, Twining and Baines, 2013). The combination, then, of a high biotic Co:Mn and a

645 lower ratio from a sedimentary source can produce the slope observed in the water column, but

646 requires remineralized dCo to be chiefly ligand-bound in order to preserve the near-crustal

647 LCo:Mn slope. The higher phytoplankton Co:Mn ratio relative to their shared sedimentary

648 source results in a nutrient trap that returns upwelled dCo to the OMZ more efficiently than dMn

649 and implies that input of dCo from the shelf is rapidly followed by biological utilization,

650 demonstrated in the transition from a dMn-like profile below the oxycline to a PO$_4$-like profile

651 above it (Fig. 10).

652

653 **4.2.2 Potential redox sensitivity of coastal cobalt sources**

654

655

656 The Co/Al ratio in buried sediments on the continental shelf can provide a coarse course measure

657 of how much Co has been released to the ocean. Sub-crustal Co/Al ratios in Peruvian sediments

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658 between 9–14° S (Böning et al., 2004) match similar measurements in Chilean OMZ sediments

659 at 36° S (Table 2, Co/Al = 1.3 ± 0.1 x 10^{-4} g g^{-1}, Table 2, Böning et al., 2009) and the Gulf of

660 California (1.4 x 10^{-4} g g^{-1}, Brumsack, 1989). The deficit between these values and continental

661 crust (2.11 x 10^{-4} g g^{-1}) implies that dissolution of crustal materials along the eastern margin

662 provides a large source of dCo and LCo to the Pacific. UltimatelyIn the absence of large

663 hydrothermal inputs (see Section 4.2.5, Swanner et al. 2014), this sourceburial of Co depleted

664 sediments on the margin is needed to balance extremely high Co/Al ratios in Pacific pelagic

665 sediments, which collect Co scavenged from the water column (e.g Dunlea et al., 2015; Goldberg

666 and Arrhenius, 1958).

667

668 In contrast to depleted Co along the South American shelf, the Co/Al ratio inin shelf sediments

669 from the western margin of the Pacific appears crustal (Table 2). Holocene records from the

670 Pearl River delta and shelf slope in the South China Sea ~20° N (Hu et al., 2012, 2013) show

671 mean Co/Al ratios of 2.2 and 2.1 x 10^{-4} g g^{-1}, respectively, similar to sediments from the Gulf of

672 Papua at 9° S (2.3 x 10^{-4} g g^{-1}, Alongi et al., 1996). Crustal Co/Al in these sedimentary systems

673 implies that most of the Co provided from fluvial sediment delivery either does not dissolve or is

674 quickly reburied by water column Mn oxidation, rates of which can be very high in estuaries and

675 coastal seas (Moffett and Ho, 1996; Moffett, 1994; Sunda and Huntsman, 1987; Sunda and

676 Huntsman, 1990).

677

678 It is likely that oxidizing conditions in the water column and surface sediments prevent limit the

679 release of cobalt on reductive dissolution on the western margin, leading to crustal Co/Al ratios

680 in shelf sediments, while suboxic conditions on the eastern margin mobilize Co, evident in

681 depleted Co/Al ratios observed there. Although sedimentary anoxia releases Co bound in Mn

682 oxides, even a thin layer of O_2 penetration into sediments results in a near-zero diffusive flux

683 into the water column (Heggie and Lewis, 1984). Indeed, El Niño-driven oxygenation events on

684 the Peru shelf are associated with deposition of Mn-oxides in shallow sediments (Scholz et al.

685 2011). Bottom water deoxygenation restores Co fluxes to the water column (Johnson et al., 1988,

686 Sundby et al., 1986), but Co is also incorporated into sulfide minerals can also precipitate,

687 analogous to the 'Goldilocks' mechanisms for benthic Fe release where flux is maximized when

688 redox conditions are low enough to promote oxide dissolution but still high enough to avoid

689 pyrite burial (into which cobalt is incorporatedand by analogy, CoS; Morse and Luther, 1999,

690 Scholz et al., 2014). CoS Cobalt burial in pyrite is evident in high Co/Al content of Black Sea

691 sediments (Brumsack, 2006) and sulfide-rich pockets of Namibian sediments near Walvis Bay

692 (2.9 ± 0.7 x 10^{-4} g g^{-1}, Borchers et al., 2005), despite more widespread Co/Al depletion in

693 suboxic (but not sulfidic) terrigenous sediments underneath the Benguela upwelling region

694 (Bremner and Willis, 1993). Prevailing suboxic conditions along the Namibian coast ultimately

695 lead to an extensive dCo, dMn, and dFe plumes that reaches across the South Atlantic basin

696 (Noble et al., 2012). Similarly, depleted sedimentary Co/Al on the Peruvian margin and high dCo

697 in the water column perhaps reflect sustained anoxia that, in the present, is unlikely outside the

698 domain of OMZs.

699

700 Altogether, the accumulating evidence that the oceans' major OMZs harbor dCo plumes (Noble

701 et al., 2012, Alhgren et al., 2014, Noble et al., in prep) indicates a strong chemical connection

702 between the efficiency of dCo sources and local redox conditions where these OMZs interact

703 with the continental margin. While reductive dissolution is the most likely mechanism at play,

whether this process predominantly occurs in estuaries, the OMZ water column, or margin sediments is presently unclear, but will ultimately dictate how the dCo source (and the resulting OMZ plumes) are affected by climate-driven changes in the size and intensity of OMZs (e.g. Scholz et al. 2011, 2014). As such, there is a significant need for future experimental and field studies that address the redox sensitivity of dCo and other metal fluxes from coastal environments.

4.2.3 Comparing coastal sources with the OMZ cobalt plume

Can a terrigenous cobalt source account for the observed OMZ plume? Because lithogenic sediments along the Peru margin are delivered primarily by rivers (Scheidegger and Krissek, 1982), we can estimate a dCo flux to OMZ waters as the product of the fluvial sediment delivery to the continental shelf and the difference in Co/Al ratios between original rocks and buried shelf sediments:

$$\text{Co flux}_{\text{suboxic}} = \left(\frac{\text{Co}}{\text{Al}}_{\text{crust}} - \frac{\text{Co}}{\text{Al}}_{\text{suboxic sediments}} \right) * \% \text{ Al} * F_{\text{fluvial}} \tag{1}$$

where F_{fluvial} is the riverine flux of terrigenous sediments from Ecuador, Peru and Northern Chile to oxygen-depleted coastlines in the ETSP. If this supply is approximately 200 MT year^{-1} (Lyle, 1981; Milliman and Farnsworth, 2011), the Co deficit in Peruvian sediments from Böning et al., 2004 corresponds to a 2.5–4.6 x 10^7 mol per year flux from the South American shelf, depending on the crustal endmember applied (upper continental crust vs. andesite, Table 2). When scaled to the size of the ETSP OMZ (2.2 x 10^6 km^3 defined at 20 μM O_2, Fuenzalida et al., 2009) a terrigenous cobalt supply of 11–21 pM year^{-1} would be expected.

727 The extent to which the coastal flux and dCo inventory are in agreement depends on the

728 residence time of OMZ waters. Models and CFC distributions from WOCE imply an

729 approximately decadal recirculation time in OMZ waters relative to mesopelagic gyre circulation

730 in the ETSP (Deutsch et al., 2001, 2011). Integrating our terrigenous Co flux estimate over 10

731 years yields an expected concentration of 120–230 pM within the OMZ. This is of similar

732 magnitude, but greater than the concentrations measured on the GP16 transect (mean of 100 ± 30

733 pM). The difference between estimated and actual dCo inventories in the OMZ is probably due

734 to upwelling and advection by surface currents, readily seen in the dCo section (Fig. 6), which

735 carries the remainder to the gyre.

736

737 **4.2.4 Comparison to atmospheric deposition**

738

739 We can compare the calculated sedimentary flux to an expected flux from aerosol dust

740 dissolution. Aeolian deposition is extremely low over the South Pacific basin (Mahowald et al.,

741 2005), except immediately offshore of Peru, where dust from the Altiplano interacts with the

742 prevailing northward winds (Prospero and Bonatti, 1969; Scheidegger and Krissek, 1982). Model

743 results (Mahowald et al., 2005) suggest that deposition does not exceed 0.5 g m^{-2} yr^{-1}, except

744 very close to the coastline. Using this estimate, crustal cobalt abundances, and the aerial extent of

745 the OMZ (9.8×10^6 km^2, Fuenzalida et al., 2009), we ~~can~~ estimate the ~~an~~ aerial flux of cobalt~~Co~~

746 from dust to be 1.4×10^6 mol ~~Co~~ per year. A 10% fractional solubility for ~~Co~~ cobalt (Shelley et

747 al., 2012) indicates a soluble cobalt flux from dust of 0.065 pM dCo year^{-1}, ~0.5 % of the

748 expected sedimentary flux. Over a decade, dust deposition accounts <-1 pM of the OMZ dCo

749 plume. dCo profiles also lack surface maxima near shore despite corresponding features for

750 dissolved Al and Mn at Stations 1 and 5 (Fig. 10, Resing et al., 2015). Fluvial sediment delivery

751 to the margin, therefore, is a much more plausible source for the elevated dCo in the ETSP OMZ.

752

753 **4.2.54 An inefficient cobalt source in hydrothermal vents**

754 Hydrothermal venting along the Eastern Pacific Rise (EPR) provides a major source of dFe and

755 dMn to the deep South Pacific (Resing et al., 2015) where nanomolar concentrations of both

756 metals were measured between 2000–3000 m at the ridge crest and concentrations exceeded

757 background values for several thousand kilometers westward. In contrast, dCo concentrations are

758 only slightly elevated at the ridge crest (Station 18, Fig. 312), reaching 36 pM at 2400m (against

759 a background of ~25 pM); at the same station, dFe and dMn both exceeded 15 nM (background

760 <1 nM, Fig. 12a)). Unambiguous hydrothermal input is evident from the LCo profile, which

761 peaks at 14 pM at the dCo maximum (Fig. 12b), roughly consistent with a 10,000-fold dilution

762 of high temperature endmember sources containing 100–1000 nM dCo (Lupton et al., 1985;

763 Metz and Trefry, 2000).

764

765 However, both dCo and LCo maxima are offset from dFe and dMn plumes. At Sstation 18, dFe

766 and dMn peak at 2500–2600 m. At this depth, LCo is undetectable and dCo values are at – or

767 slightly lower than – background levels (Fig. 12b), suggesting that Mn and/or Fe scavenging in

768 the heart of the hydrothermal plume has removed most of the hydrothermal Co from the water

769 column before being transported away from the ridge crest (Fig. 12). Indeed, Co is strongly

770 associated with Mn phases in near-axis metalliferous sediment in the EPR at 14° S (Dunk and

771 Mills, 2006). The position of the LCo maximum above the dMn and dFe maxima probably

772 reflects lower scavenging rates outside the main plume, which may spare a fraction of the

773 hydrothermal Co source from an otherwise immediate and total removal. Even without

774 scavenging losses, global hydrothermal Co fluxes (2.2 Mmol year^{-1}; Swanner et al., 2014) are

775 10–25x less than our estimated source from the Peru Shelf alone, highlighting the importance of

776 upper ocean sources in maintaining the dCo inventory.

777

778 **4.35 Cobalt scarcity in the euphotic zone**

779 **4.3.1 The South Pacific gGyre**

780 The combination of eastern boundary upwelling and a continental source produces large dCo

781 gradients across the surface of the South Pacific Ocean (Fig. 6a13). Westward, decreasing

782 surface dCo results from phytoplankton uptake and export, reflected in strong correlations with

783 PO$_4$, as well as mixing with low dCo waters from the subtropical gyre. It is interesting to note

784 that the intercept for the dCo:PO$_4$ relationship is negative (-12.8 ± 2.6 μM M^{-1}, Fig. 7b); cobalt

785 was depleted before PO$_4$. This is opposite to what was observed in the Sargasso Sea, where

786 extreme PO$_4$ scarcity results in a positive dCo:PO$_4$ intercept (Jakuba et al., 2008). The dCo

787 nutricline in the South Pacific gyre (~200 m, Figs. 3, 6) is also deeper than corresponding

788 features in the North and South Atlantic (Noble et al., 2012; Noble and Saito, in prep). Because

789 winter mixed layers in the tropical South Pacific generally does not exceed 100 m and strong

790 haloclines separate the oxygen minimum layer from the surface (Fiedler and Talley, 2006),

791 convective overturn does not reach the dCo nutricine at 150–250 m. Low vertical cobalt supply

792 makes the South Pacific gyre an interesting counterpoint counterpart to the Sargasso Sea, which

793 experiences deep winter mixed layersmixing and higher dCo (10–30 pM, Dulaquais et al.,

794 2014b; Jakuba et al., 2008; Noble and Saito, in prep), and emphasizes the importance of lateral

795 supply mechanisms, especially eastern boundary upwelling, in maintaining the surface dCo

796 inventory of the tropical Pacific (Fig. 6, Saito et al., 2004).

797

798 While productivity in the South Pacific is thought to be limited by scarcity of iron and nitrogen

799 (Moore et al., 2013; Saito et al., 2014), the extremely low dCo measured here implies that it may

800 be important as well. Because marine cyanobacteria such as *Prochlorococcus* and

801 *Synechococcus* have an absolute Co requirement (Saito et al., 2002; Sunda and Huntsman, 1995),

802 they are vulnerable to limitation. Indeed, a *Synechococcus* bloom in the Costa Rica Dome was

803 found to be co-limited by both iron and cobalt (Saito et al., 2005). Despite dCo concentrations

804 below 10 pM (sometimes below the 3 pM detection limit), the South Pacific gyre contains a

805 significant *Prochlorococcus* population – evident in the high proportion of divinyl chlorophyll A

806 to total chlorophyll (Fig. 13ab). As LCo was undetectable beyond 100° W, biological uptake

807 must occur either by accessing strongly bound dCo or through fast recycling of LCo at very low

808 steady-state concentrations. On GP16, particulate Co concentrations in the upper 50 m were

809 steady (3.5 ± 1.2 pM) and mostly reflect Co bound in biomass (Ohnemus et al., In Press),

810 sometimes rivaling and sometimes equaled dissolved cobalt concentrations (Fig. 13b). Compared

811 to low pCo:dCo ratios observed in the South Atlantic (<1:12, Noble et al., 2012), the high ratio

812 in the South Pacific gyre (~1:3, Fig. 13ba) indicates that resident *Prochlorococcus* are extremely

813 well-adapted to widespread dCo scarcity and that efficient recycling of biogenic pCo may be

814 crucial to survival of *Prochlorococcus* and other cyanobacteria (e.g. *Synechococcus*, Ahlgren et

815 al. 2014) in the face of widespread dCo scarcity. y.

816

817 **4.3.2 Depletion of labile dissolved cobalt in the Peru Upwelling Ecosystem**

818 Unlike its near uniform relationship with dCo in the underlying OMZ, LCo measured on GP16 is

819 low relative to dCo in the surface ocean (0–50 m), especially along the Peru Margin (Figs. -76a,

820 13cb, 13c). This might result either from microbial production of cobalt ligands – as observed in

821 a *Synechococcus*-dominated community in the Costa Rica Dome (Saito et al., 2005) and with

822 cultured *Prochlorococcus* strains (Saito et al. 2002) – or if LCo is the preferred species for

823 uptake. The latter has been demonstrated in culture with model eukaryotic algae (Sunda and

824 Huntsman, 1995), where free Co ion is acquired by high affinity Zn-transporters. Because the

825 Peru upwelling region is dominated by diatoms (Bruland et al., 2005), preferential uptake of free

826 Co ion by these organisms is realistic and is corroborated by a strong correlation between LCo

827 and dissolved silicate (Si) in the upper 50 m of the section (R^2 = 0.90, Fig. 7c). As a result of

828 diatom-driven export, LCo in shelf surface waters is nearly depleted (1–12 pM) despite high

829 concentrations of dCo (40–80 pM, Fig. 13c). Very low surface LCo at 12° S on GP16 contrasts

830 with previous observations showing high concentrations of LCo in the Peru upwelling region

831 during August–September 2000 (Saito et al., 2004). Between 5–10° S, much higher surface dCo

832 was measured in freshly upwelled waters (up to 315 pM) and dCo was >50 % labile in surface

833 transects (Saito et al., 2004). Surface dFe during August–September 2000 was also higher

834 between 5–10° S than on GP16 at 12° S (Bruland et al., 2005; Resing et al., 2015). Decreasing

835 surface dFe from North to South followed decreasing gradients in shelf width and fluvial

836 sediment supply (Bruland et al., 2005; Milliman and Farnsworth, 2011), implying that the high

837 dFe was due to stronger benthic sources to the North. Because coastal sources are expected to

838 provide labile cobalt (e.g. Fig 11), the high concentrations of LCo measured between 5–10° S

839 during August–September 2000 indicate a similar gradient in coastal dCo input and LCo

840 availability in surface waters.

841

842   Spatial and temporal variability of margin dCo sources may ultimately affect carbon flow

843   through the Peru upwelling ecosystem. Considering the very low dissolved Zn in surface waters

844   on GP16 (<100 pM east of 90° W, S. John personal communication) and that >95 % of the dZn

845   is typically complexed by organic ligands (Bruland, 1989), coastal diatoms in the off of Peru

846   upwelling region may be subject to diffusion limitation when free Zn ion falls below a 1–10 pM

847   threshold (Sunda and Huntsman, 1992). Because Co can replace Zn in carbonic anhydrase

848   enzymes (Sunda and Huntsman, 1995; Yee and Morel, 1996), LCo supplied from the margin

849   may maintain fast rates of carbon fixation and export in the Peru Upwelling region despite low

850   dZn. The relatively low concentrations measured on GP16, however, imply that the LCo supply

851   may not always be sufficient.

852

853   **5. Conclusions**

854   A schematic of the cobalt cycle in the Eastern Tropical South Pacific Ocean – and how these

855   processes lead to covariation of dissolved cobalt with O_2 and PO_4 – is shown in Figure 14. High

856   dCo and LCo on the Peru shelf match depleted Co content reported in Peru shelf sediments and

857   indicate a large source to the water column (Böning et al., 2004). Correlations between dMn and

858   LCo in anoxic shelf waters, and crust-like Co/Al ratios in oxic western boundary sediments

859   suggest that margin cobalt sources are redox sensitive and that the sustained presence of the

860   OMZ on the Peru margin amplifies coastal Co fluxes. The high dCo within the OMZ also leads

861   to a large flux to the surface ocean by upwelling along the Peru margin, where it is readily

862   accessed by phytoplankton. The significance of cobalt as a micronutrient is emphasized by

863   strong correlations with phosphate throughout the surface ocean.Strong correlations with

864 ~~phosphate across the surface ocean emphasize its significance as a micronutrient. Preferential~~

865 ~~uptake of LCo over the Peru shelf by diatoms generates a linear relationship with silicate and Co~~

866 ~~may be critical to sustaining carbonic anhydrase activity and CO_2 fixation during blooms.~~

867

868 The basin scale association between high dCo and low O_2 throughout the GP16 section testifies

869 to the importance ~~of redox chemistry and~~of remineralization in maintaining the dCo distribution

870 in the Eastern South Pacific (Fig. 14). ~~High dCo and LCo on the Peru shelf match depleted Co~~

871 ~~content reported in Peru shelf sediments and indicate a large source to the water column (Böning~~

872 ~~et al., 2004). Correlations between dMn and LCo in anoxic shelf waters, and crust-like Co/Al~~

873 ~~ratios in oxic western boundary sediments suggest that margin cobalt sources are redox sensitive~~

874 ~~and that the sustained presence of the OMZ on the Peru margin amplifies coastal Co fluxes.~~

875 Additionally, low oxygen ~~in offshore OMZ waters~~ suppresses particulate Mn accumulation and

876 Co scavenging, ~~evident in isopycnal dCo-salinity relationships~~contributing to the OMZ cobalt

877 plume. ~~When mixing introduces sufficient O_2 to stabilize Mn oxides, high particulate Co:P ratios~~

878 ~~in the mesopelagic accompany 10-fold higher particulate Mn.~~ Scavenging in oxic mesopelagic

879 waters limits the full return of Co to the dissolved phase during remineralization, resulting in low

880 dissolved Co:P ratios relative to ~~that~~ biomass exported from the euphotic zone ~~(Fig. 14)~~.

881 Oxidative scavenging also seems to limit the flux of Co from hydrothermal venting over the East

882 Pacific rise, further emphasizing the Peru margin as the most important Co source to the South

883 Pacific.

884

885 ~~The high dCo within the OMZ also leads to a large flux to the surface ocean by upwelling along~~

886 ~~the Peru margin, where it is readily accessed by phytoplankton. Strong correlations with~~

887 ~~phosphate across the surface ocean emphasize its significance as a micronutrient. Preferential~~

888 ~~uptake of LCo over the Peru shelf by diatoms generates a linear relationship with silicate and Co~~

889 ~~may be critical to sustaining carbonic anhydrase activity and CO_2 fixation during blooms.~~ Given

890 that deep nutriclines in the South Pacific Gyre limit dCo supply from vertical mixing outside of

891 the upwelling zone, phytoplankton Co nutrition depends largely on lateral supply from the

892 Eastern Margin.

893

894 Ultimately, the dCo inventory in the South Pacific – and its availability to surface phytoplankton

895 – may be changing considerably as the size ~~and intensity~~ of the OMZ fluctuates. Recent warming

896 and stratification appear to have expanded the volume of low oxygen waters in the tropics

897 (Stramma et al., 2008, 2010). As such, dCo inventories may increase as lower O_2 hinders

898 mesopelagic Mn oxide production and scavenging. However, decreased wind-driven upwelling

899 and carbon export may cause anoxic waters along the shelf to contract (Deutsch et al., 2011,

900 2014) and decrease the efficiency of the coastal dCo source ~~Co flux from coastal sediments~~.

901 Changes in the dCo inventory then depend on the relative redox sensitivities of ~~the~~ margin Co

902 sources versus offshore scavenging in the mesopelagic, neither of which ~~are~~ is well understood.

903 Considering the 100–200 year residence time of Co in the ocean (Saito and Moffett, 2002),

904 feedbacks on the surface dCo supply may manifest more quickly than for other nutrients and

905 may alleviate or exacerbate any existing Co limitation. Improved definition of biological Co

906 limitation thresholds and efforts to reconstruct the Co cycle in past climates may resolve whether

907 future changes in OMZ structure will have meaningful impacts on phytoplankton nutrition in the

908 coming century.

909

Author Contributions

NJH, DCO and JAR participated on the EPZT cruise. NJH measured dCo and LCo. JAR

measured dMn; DCO and BST measured particulate Co, Mn, and P. NJH and MAS prepared the

manuscript with contributions from all authors.

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1193   **Table 1.** Blanks and standards used during analyses.

		dCo, pM	+/-	n	Consensus
At sea	Blank	3.7	1.2	28	
Oct – Dec,	Lab SW*	4.5	2.1	28	
2013	D1	48.5	2.4	3	46.6 +/- 4.8
At WHOI,	Blank	4.7	1.4	12	
Sept – Nov,	GSP	2.5	2.0	10	4.9 +/- 1.2**
2014					
	D2	45.0	2.7	7	46.9 +/- 3.0
	GSC	77.7	2.4	4	***

1194   *~~Collected from~~ South Pacific surface seawater, collected Nov. 2011

1195   **Refers to SAFe standard S, ~~which was~~ collected at the same location as GSP

1196   ***No consensus

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1199   **Table 2.** Co/Al ratios in sediments from different redox regimes.

Location	Co-/-Al x 10^{-4} (g g^{-1} $^{-1}$)		Reference
Crust			
Upper continental crust	2.11		McLennan 2001
Andesitic crust	2.63		Taylor and McLennan 1995
Eastern Boundary sediments			
Peru Upwelling Sediments	1.2 ± 0.3	9–14° S	Boning et al. 2004
Chile upwelling Sediments	1.3 ± 0.1	36° S	Boning et al. 2009
Gulf of California	1.4	22–30° N	Brumsack 1989
Namibian Shelf	1.0 ± 0.3	17–25° S, 'Terrigenous'	Bremner and Willis 1993
Sulfidic Sediments			
Namibian diatom belt	2.9 ± 0.7	Near Walvis Bay, 22.5° S	Borchers et al. 2005
Black Sea	3.8–6.2		Brumsack 2006
Western Boundary Sediments			

Papua New Guinea	2.3	8° S, Gulf of Papua	Alongi et al. 1996
Pearl River Delta	2.2 ± 0.4	22° N, (10–0 ka)	Hu et al. 2013
South China Sea Shelf Slope	2.1 ± 0.2	20° N, 2037m (14–0 ka)	Hu et al. 2012
Deep Ocean Sediments			
South Pacific Gyre	35 (2.9–101)	22° S–32° S, 100–0 Ma	Dunlea et al. 2015
Pelagic Pacific	17 (2–58)	50° N–20° S	Goldberg and Arrhenius 1958

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Figure Captions

Figure 1. The GP16 transect in the tropical South Pacific. Red circles indicate sampling stations. Dissolved oxygen at a depth of 300 m from the WOCE dataset is plotted in blue and 10 μM contours are shown between 0–60 μM O_2. Station number increases sequentially westward, with the exception of Station 1.

Figure 2. Signal processing of voltammetry scans. Varying instrumental noise imprinted negative current excursions during measurement and necessitated data smoothing to correctly ~~integrate~~ measure the $Co(DMG)_2$ reduction peak at -1.15 V. For mild (a) and moderate (b) noise levels, a 2nd order, 17-point smoothing was applied (red line, 97 % of scans). Increases in noise caused this routine to overestimate peak height (c, red line) and a first order, 13-point smoothing was applied instead (~3 % of scans, blue line).

Figure 3. Profiles of dissolved cobalt (dCo, closed circles), labile dissolved cobalt (LCo, open circles) and O_2 (grey lines) across the South Pacific. Upper panels show a 0–1000 m depth range; bottom panel show full profiles. dCo and LCo are highest close to the Peru Margin (Station 1) and decrease westward. O_2 follows the opposite trend. The small peak at 2400 m at Station 18 shows peak hydrothermal input from the East Pacific Rise. Note that the dCo and LCo scales in the upper panel are adjusted to highlight gradients and differ from the lower panels.

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Figure 4. Dissolved oxygen (a), dissolved cobalt (b) and labile dissolved cobalt (c) sections along GP16, projected on a longitudinal axis. Note high dCo and LCo stem from the Peru margin and overlap with the low O_2. Interpolations were made using Ocean Data View with DIVA gridding, with negative gridded values suppressed. The signal to noise ratio was set to 15 for dissolved cobalt and labile dissolved cobalt. Signal to noise for O_2 was set to the default, 50.

Figure 5. Coupling between dissolved cobalt with O_2 (a), AOU (b), and PO_4 (c). Below 200 m (red circles), dCo shows a decreasing linear trend with dissolved oxygen that is obscured upon conversion of O_2 to apparent oxygen utilization, AOU, and a weak relationship with PO_4. In the surface ocean (upper 0–50200 m, (cyanblue circles), dCo and PO_4 are strongly coupled but dCo shows no relationship with O_2 or AOU. Samples from 50–200 m are plotted in blue. Trend lines in (c) show least-squares regressions of dCo and PO_4. (0–50 m, cyan; 50–200 m, blue; 200–1000 m, red). Also plotted is the median best fit for 0–50 m in particulate Co:P ratio for 0–50 m (146 μM M^{-1}, dotted line).; Major 0–50 m dissolved Co:P (69 μM M^{-1}, blue line, see Fig. 7b) and 200–1000 m regression for dissolved Co:P (16 μM M^{-1}, red line). pProcesses affecting these plots are described in vector legends.

Figure 6. Dissolved cobalt (a), labile dissolved cobalt (b), and particulate cobalt (c) gradients in the upper 500 m of the ETSP. White lines in both panels show dissolved PO_4 contours at 0.5 μM increments. Interpolation was conducted using weight averaged gridding with 40 and 46 ‰ length scales in the x and y directions, respectively.

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1244 **Figure 7**. (a) The relationship between dissolved cobalt (dCo) and labile cobalt (LCo) in the

1245 South Pacific. LCo increases linearly with dCo with a slope of 0.33 (black dots, $R^2 = 0.88$),

1246 except for the upper 50 m (red dots), where samples fall below this trend due to preferential

1247 depletion of LCo by phytoplankton. (b) In the 0–50 m range, dCo strongly correlates with

1248 phosphate ($R^2 = 0.89$). (c) LCo is preferentially removed from surface waters (0–50 m) and

1249 tracks silicate ($R^2 = 0.90$).

1250

1251 **Figure 8**. Transition in dCo cycling at the OMZ boundary in the upper South Pacific

1252 thermocline. (a) Isopycnal windows centered at $\sigma_\theta = 26.2 \pm 0.1$ kg m^{-3} (circles) and $\sigma_\theta = 26.4 \pm$

1253 0.1 kg m^{-3} (triangles) show PO$_4$-coupled cycling in oxygenated waters (blue) but not in OMZ

1254 waters with $O_2 < \leq 20$ μM O_2 (red). (b) In the OMZ, dCo follows salinity, indicating mixing

1255 between a high dCo endmember at a salinity of 35.0 and a fresher water mass that is low in dCo.

1256

1257 **Figure 9**. Redox control of Co and Mn scavenging. Within mesopelagic waters ($\sigma_\theta = 26.2$–27.0

1258 kg m^{-3}, mean depth of 300 m), high O_2 in ventilating water masses result in a sharp redox

1259 boundary at the edge of the OMZ (red circles, scale in μM). Particulate Mn (pMn) increases

1260 across the oxic/anoxic boundary at 100° W (blue circles, in nM) and imply stabilization of Mn

1261 oxides. Both pMn:pP and pCo:pP (cyan and pink circles, respectively; units are M M^{-1}) increase

1262 across the OMZ boundary, exceeding predicted values from remineralization of biogenic

1263 material from the surface ocean (1.26 x 10^{-3} mean pMn:pP and 1.57 x 10^{-4} pCo:pP for 0–50 m

1264 (M M^{-1}), cyan and pink lines, respectively). Dissolved phase dCo:dPO$_4$ (black circles) and

1265 LCo:PO$_4$ (white circles) also decrease west of the OMZ boundary show scavenging of the dCo

1266 and LCo in the mesopelagic (units are M M^{-1}).

1267

1268 **Figure 10.** Profiles of dissolved cobalt (dCo, black), PO_4 (red) and dMn (blue) over the Peru

1269 shelf at 12° S. The oxycline (grey bar, defined by the first sample where $O_2 \leq 10$ μM) marks the

1270 transition between the OMZ and oxygenated surface waters. Station 2 is the closest to the coast.

1271 Note the similarity between dCo and PO_4 above the oxycline and the transition to a dMn-like

1272 profile beneath~~ it~~.

1273

1274 **Figure 11.** Cobalt and Mn in the Peru shelf OMZ (GP16 Stations 1–5, $O_2 \leq 20$ uM). Dissolved

1275 cobalt (dCo, closed circled) and labile cobalt (LCo, white) follow positive linear relationships

1276 with dMn. The LCo slope (18 mM M^{-1}) approximates the Co:Mn ratio in upper continental crust

1277 and Andesite (red and pink lines 21 and 26 mM M^{-1}, respectively), suggesting it derives from a

1278 ~~shelf~~ crustal source. The mean pCo:pMn ratio from phytoplankton dominated particles collected

1279 in the upper 40 m over the shelf (blue line, 105 mM M^{-1}) is greater than dCo:dMn slope (42 mM

1280 M^{-1}), indicating that dCo and dMn concentrations in the Peru shelf OMZ represent a combination

1281 of biomass remineralization and sedimentary input.

1282

1283 **Figure 12.** Profiles from Station 18 at the East Pacific Rise ridge crest at 113 °W, 15 °S. (a) dMn

1284 (blue lines) and dFe profiles (red) replotted from Resing et al. 2015 clearly show hydrothermal

1285 input. Grey shading below 2250 m indicates area of hydrothermal influence where dFe and dMn

1286 are >1 nM. (~~b~~a) Dissolved cobalt (dCo, black circles) and labile cobalt (LCo, white) in the East

1287 Pacific Rise hydrothermal plume.

1288   ~~Profiles are from Station 18 at the EPR ridge crest at 113 °W. (b) dMn (blue lines) and dFe~~

1289   ~~profiles (red) replotted from Resing et al. 2015 clearly show hydrothermal input. Grey shading~~

1290   ~~below 2250 m indicates area of hydrothermal influence where dFe and dMn are >1 nM.~~

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1292   **Figure 13.** (a~~b~~) The ratio of divinyl chlorophyll A to total chlorophyll (green circles), an

1293   indication ~~proxy for~~of *Prochlorococcus* abundance relative to other phytoplankton.~~,~~ (b~~a~~) The

1294   particulate to dissolved ratio of cobalt (pCo:dCo, in M M^{-1}, pink circles) in near-surface samples

1295   (0–50m) measured on GP16; a value of 1 indicates equal concentrations in each phase. ~~(b) The~~

1296   ~~ratio of divinyl chlorophyll A to total chlorophyll (green circles), a proxy for Prochlorococcus~~

1297   ~~abundance.~~ (c) The near-surface distribution of dissolved cobalt (dCo, black circles) and labile

1298   cobalt (LCo, white circles), showing higher concentrations near the Peru margin (<80° W) and

1299   very low dCo to the west.

1300

1301   **Figure 14.** ~~S~~A ~~s~~chematic cross-section of the cobalt cycle in the Eastern Tropical South Pacific.

1302   Black arrows describe idealized physical circulation, showing upwelling near the Peru margin,

1303   advection westward and subduction in the South Pacific gyre. Biological Co export is shown in

1304   the red-hashed arrows, and solid and dashed red arrows show remineralization and scavenging

1305   respectively. The margin source is shown as a red-outlined arrow. These vectors are also plotted

1306   on idealized oxygen and phosphate axes, using the same color scheme, to show how these

1307   processes appear in Co:O$_2$ and Co:PO$_4$ space.