

## Cobalt and nickel in the Peru upwelling region: A major flux of labile cobalt utilized as a micronutrient

Mak A. Saito and James W. Moffett

Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA

Giacomo R. DiTullio

Grice Marine Laboratory, Department of Biology, College of Charleston, Charleston, South Carolina, USA

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[1] The geochemistry of cobalt in the Peru upwelling region is dominated by its importance as a micronutrient. A large and previously undocumented flux of labile cobalt behaved as a micronutrient with correlations with major nutrients (nitrate, phosphate;  $r^2 = 0.90, 0.96$ ) until depleted to  $\leq 50$  pM of strongly complexed cobalt. Co:P utilization ratios were an order of magnitude higher than in the North Pacific, comparable to utilization rates of zinc in other oceanic regions. Cobalt speciation measurements showed that available cobalt decreased over 4 orders of magnitude in this region, with shifts in phytoplankton assemblages occurring at transitions between labile and nonlabile cobalt. Only small changes in total dissolved nickel were observed, and nickel was present in a labile chemical form throughout the region. In the Peru upwelling region, cobalt uptake was highest at the surface and decreased with depth, suggesting phytoplankton uptake was a more important removal mechanism than co-oxidation with microbial manganese oxidation. These findings show the importance of cobalt as a micronutrient and that cobalt scarcity and speciation may be important in influencing phytoplankton species composition in this economically important environment. *INDEX TERMS*: 1030

Geochemistry: Geochemical cycles (0330); 1050 Geochemistry: Marine geochemistry (4835, 4850); 1065

Geochemistry: Trace elements (3670); 4279 Oceanography: General: Upwelling and convergences;

*KEYWORDS*: cobalt speciation, nickel, Peru upwelling, Pacific, phytoplankton

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### 1. Introduction

[2] The waters of the Peru upwelling regime are among the most productive in the world, with important economic value associated with the fishing industry [Nixon and Thomas, 2001]. Recent fieldwork has shown that the primary productivity of this region can be limited by iron: bottle incubation studies showed stimulation of phytoplankton by iron, and total dissolved iron was as low as  $\sim 0.1$  nM or less (K. W. Bruland, et al., Iron, macronutrients and diatom blooms in the Peru upwelling regime: Brown and blue waters of Peru, submitted to *Marine Chemistry*, 2004) (hereinafter referred to as Bruland et al., submitted manuscript, 2004) [Hutchins et al., 2002]. It is believed that the combination of upwelled water with high major nutrients and low iron, as well as limited iron inputs from riverine sources, creates the conditions of iron limitation here and in other upwelling systems (e.g., California upwelling) [Hutchins and Bruland, 1998]. Prior to this study, there has been little to no focus on the

biogeochemical characteristics of cobalt in upwelling regions.

[3] The geochemistry of cobalt has several similarities to that of iron. In particular, cobalt concentrations also tend to be extremely low in seawater, and both elements do not accumulate in deepwaters with remineralization from sinking particles and entrainment in thermohaline circulation as major nutrients do. Particle scavenging of iron and cobalt is believed to result in the consistently low deepwater concentrations throughout the major ocean basins [Saito and Moffett, 2002; Wu and Boyle, 2002]. Cobalt also has similar redox chemistry to that of iron, existing in either the +2 or +3 under typical environmental  $E_H$  and pH conditions, and with both elements being highly insoluble in the +3 state due to precipitation of hydrolysis species.

[4] Despite these similarities, we believe that the importance of cobalt as a micronutrient is more subtle than that of iron, to the extent that until very recently the prevailing view was that nonbiological processes dominate the geochemical cycling of cobalt [Johnson et al., 1988]. Cobalt is clearly used by phytoplankton as a micronutrient in culture studies, and its abundance in the environment is so

low that it may become limiting to certain phytoplankton groups, thereby influencing community composition. The geochemistry of cobalt has the combined complexities of (1) the possible biochemical substitution of Co with Zn or Cd, and (2) the influence of the chemical speciation of each on the biological availability to phytoplankton. While the biological influence of elements such as zinc and copper have been examined in the surface ocean environment [Coale, 1988, 1991; Coale *et al.*, 2003; Crawford *et al.*, 2003; Franck *et al.*, 2003], there is little published data examining the importance of cobalt as a micronutrient in oceanic regimes. There are some organisms that can substitute all three of these elements (some diatoms and perhaps *E. huxelyii*) [Lane and Morel, 2000; Morel *et al.*, 1994; Price and Morel, 1990], yet there are also others that cannot, in particular the cyanobacteria [Saito *et al.*, 2002; Sunda and Huntsman, 1995], and some strains of diatoms [Timmermans *et al.*, 2001].

[5] The chemical speciation of metals in seawater is believed to be of fundamental importance in determining metal bioavailability to phytoplankton. However, owing to the difficulty of making metal speciation measurements, data sets tend to be small and are often limited to a few vertical profiles. Methods to measure cobalt speciation in oceanic environments were recently developed and showed cobalt speciation to be dominated by organic complexation in the Atlantic [Ellwood and van den Berg, 2001; Saito and Moffett, 2001]. Previous studies of nickel speciation have shown nickel to be only partially complexed by strong organic ligands in coastal and open ocean environments [Achterberg and van den Berg, 1997; Donat and Bruland, 1988; Donat *et al.*, 1994; Zhang *et al.*, 1990]. The simultaneous measurement of cobalt and nickel speciation in this study allows us to test hypotheses regarding the specificity of these ligand(s) for each metal, as well as the potential contribution of these elements from sediment fluxes and upwelled intermediate waters. Here we present a large cobalt and nickel speciation data set and corresponding phytoplankton assemblage data across the chemical gradients associated with the Peru upwelling regime.

## 2. Methods

### 2.1. Total Cobalt Analysis

[6] Total dissolved cobalt was measured as previously described [Saito and Moffett, 2002]. Analysis was performed at sea within 1 week of collection in a laminar flow bench and positive pressure clean bubble. Briefly, samples were collected from approximately 8–10 m depth from a trace metal clean Teflon pumping system, or by Teflon coated 30-L Go-Flo bottles. All samples were filtered immediately through a 0.4- $\mu\text{m}$  filter and stored in Teflon or LDPE (low-density polyethylene) bottles at 4°C in darkness until analysis. All plasticware was rigorously cleaned in citranox detergent overnight followed by a 10% hydrochloric acid leach at 60°C for 48 hours and a soak in dilute ultrapure HCl (pH 2). For total dissolved cobalt, samples were UV-irradiated (Ace Glass) for 3 hours  $\pm$  5 min in closed 15-mL quartz tubes. Previous

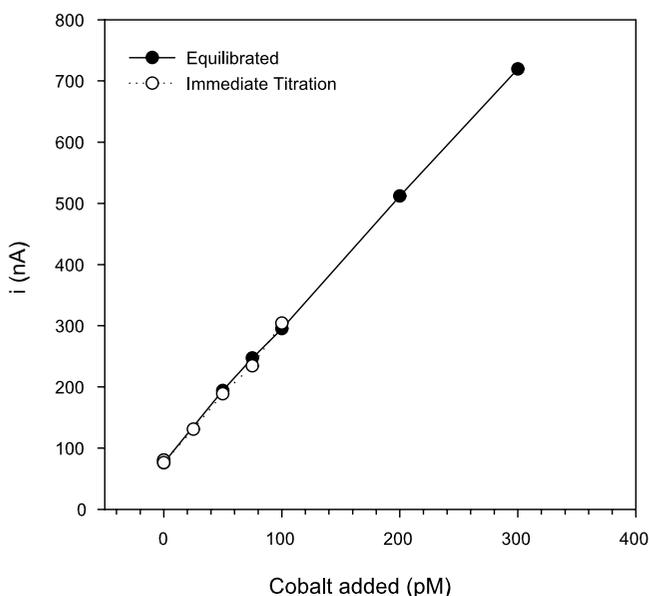
studies have shown that UV-irradiation at neutral pH does not decrease recovery, and that running freshly collected samples at ambient pH prevents blank problems associated with acidification and neutralization [Saito and Moffett, 2002; Vega and van den Berg, 1997]. Purified dimethylglyoxime (DMG), N-(2-hydroxyethyl)piperazine-N-(3-propanesulfonic acid) (EPPS), and sodium nitrite were added to 8.50 mL of UV-digested seawater in a Teflon analysis vessel for a final concentration of 0.2 mM, 2.5 mM, and 0.225 M, respectively, in a final volume of 10 mL. After a 3-min  $\text{N}_2$  purge (99.999% purity), and a 90-s  $-0.6\text{-V}$  deposition potential, the sample was scanned in triplicate on an Eco-Chemie  $\mu\text{Autolab}$  and Metrohm 663 electrochemical system. The voltammetric scan ranged from  $-0.6$  to  $-1.4$  V at 10 V/s in linear sweep mode. Cobalt nitrate additions of 25 pM were made from dilutions of a certified cobalt standard (Fisher). Cobalt blanks were determined for each batch of reagents used ( $\sim 6$  pM), as previously described [Saito and Moffett, 2001], and were subtracted from measured values.

### 2.2. Cobalt and Nickel Speciation Analysis

[7] Cobalt speciation was measured using a previously developed method [Saito and Moffett, 2001] and is presented here as a concentration of labile cobalt where labile refers to cobalt that was exchangeable with 50  $\mu\text{M}$  of the strong synthetic cobalt ligand dimethylglyoxime (DMG) after overnight equilibration (equations (1) and (2)).



where CoL refers to the cobalt bound to a strong natural ligand of unknown structure. CoHDMG<sub>2</sub> adsorbs to the mercury drop during the deposition period and is reduced during the negative scan, while CoL and Co<sup>2+</sup> do not react with the drop under these conditions, allowing the equilibrium between chemical species to be analyzed. The conditional stability constant for CoHDMG<sub>2</sub> in seawater was previously determined to be  $10^{11.5 \pm 0.3}$  at pH 8.0 [Saito and Moffett, 2001]. Using the experimental conditions described here, cobalt speciation was measured with a ligand conditional stability constant detection window of  $10^{12.2}$  to  $10^{14.2}$  [Saito *et al.*, 2004]. Filtered samples were equilibrated at room temperature overnight in Teflon bottles with the DMG. Labile cobalt and nickel were measured using samples equilibrated overnight with DMG addition. Standard additions of cobalt (25 pM) and then nickel (1 nM) were added to the sample after triplicate analysis of the initial sample with no metal added. Full titrations, where samples were equilibrated overnight with both DMG and cobalt additions, were conducted on selected samples and yielded results similar to that of the nonequilibrated cobalt standard additions used for labile metal determination. A representative cobalt speciation titration with both the labile cobalt titration (immediate cobalt additions) and full titration (equilibrated cobalt additions) is shown in Figure 1. Unlike our previous studies in the oligotrophic Sargasso Sea, changes in slope were not observed between



**Figure 1.** A representative titration of cobalt speciation from the Peru upwelling region. A filtered sample from 9.76°S, 81.59°W was equilibrated with DMG and cobalt while at sea. The equilibrated line represents overnight equilibrations of 50  $\mu$ M DMG with cobalt additions. The immediate titration line represents a sample equilibrated overnight with DMG and no added cobalt, which was then titrated with cobalt while in the electrode cup. Blank and dilution corrections are then applied to the calculated labile cobalt concentration.

equilibrated titrations and direct additions. Linear regressions of the metal titrations were then used to calculate the labile fraction of metal, defined as the unbound fraction remaining after equilibration with the strong synthetic added ligand DMG. In order to maximize geographical coverage, the majority of samples had only the zero metal added treatment equilibrated with DMG, and the metals (Co, Ni) were titrated in during analysis, allowing determination of labile cobalt and nickel but not the conditional binding constants of those ligands.

### 2.3. Pigment and Nutrient Analyses

[8] HPLC pigments were analyzed as previously described [DiTullio and Geesey, 2002], and the percentage of total Chl *a* that was allocated to various algal taxa was determined using the ChemTax matrix factorization program [DiTullio et al., 2003; Mackey et al., 1996; Bruland et al., submitted manuscript, 2004]. Major nutrients were analyzed at sea on a Lachat Quick Chem autoanalyzer (Bruland et al., submitted manuscript, 2004).

### 2.4. Cobalt Uptake Experiments

[9] Cobalt uptake measurements were performed using unfiltered water from Go-Flo casts at 81.6°W, 9.8°S on 16 September 2000. Seawater samples were amended with tracer concentrations (<0.4 pM) of  $^{57}\text{Co}$  (Isotope Products Laboratories) and incubated for 7 hours during the daytime

in an on-deck incubator attenuated with blue gel (Rosco, 35% transmittance) in trace metal clean 250-mL polycarbonate bottles sealed in heat-seal plastic bags. A pre-equilibrated  $^{57}\text{Co}$  working stock made in filtered surface seawater was used to spike experimental bottles. Triplicate bottles were used for each depth, and 100 mL of sample was filtered onto a 0.2  $\mu\text{m}$  polycarbonate filter from each depth. Samples were counted on a germanium detector (Canberra) to <5% counting error.

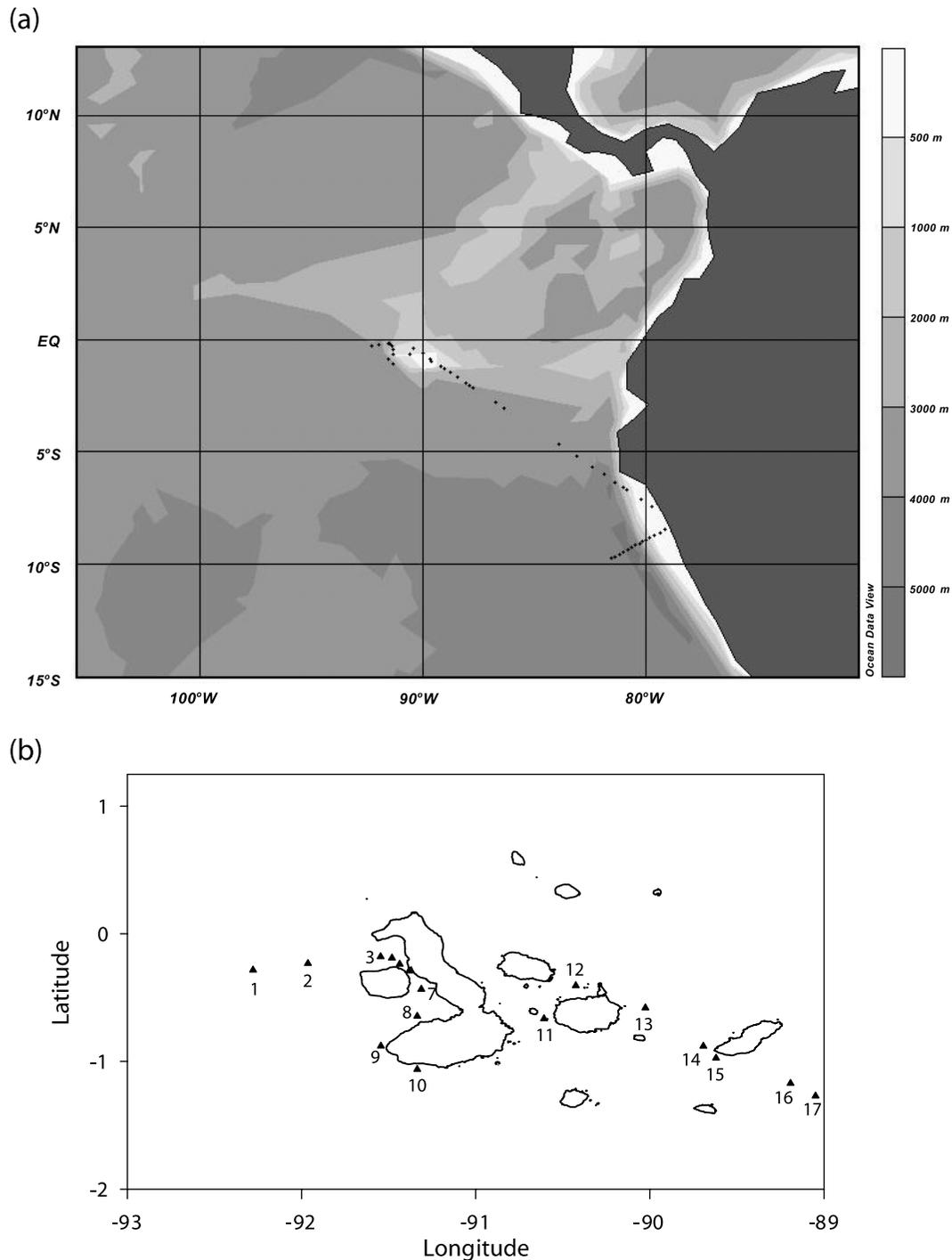
## 3. Results and Discussion

### 3.1. Cobalt and Nickel Surface Transects

[10] Total dissolved and speciation measurements of cobalt and nickel were made on two surface transects in the Peru upwelling region. The first began in equatorial Pacific waters west of the Galapagos Islands, transecting through the islands, and continued southeast to the Peru coastline (Figure 2, northern transect). The second transect ran east-west from the shelf extending offshore within the Peru upwelling region (Figure 2, southern transect), and will be discussed later in the context of the cobalt uptake experiments (section 3.6). On the northern transect, we observed a large increase in total dissolved cobalt as we moved closer to the source of the Peru upwelling waters (Figure 3), as well as a major change in cobalt speciation from strongly complexed cobalt in the open ocean area to the predominantly labile cobalt in the upwelled waters. Total dissolved cobalt increased by more than sixfold across this region, while total dissolved nickel concentrations only varied slightly (Figure 4). However, the nickel peaks in Figure 4 also coincided with cobalt peaks, (e.g., 88.1°W, 86.8°W, and 81.0°W). Nickel speciation measurements showed nickel to be primarily in a labile form throughout this transect (Figure 4).

### 3.2. Correlations Between Cobalt and Major Nutrients: Redfieldian Analysis and Possible Causes

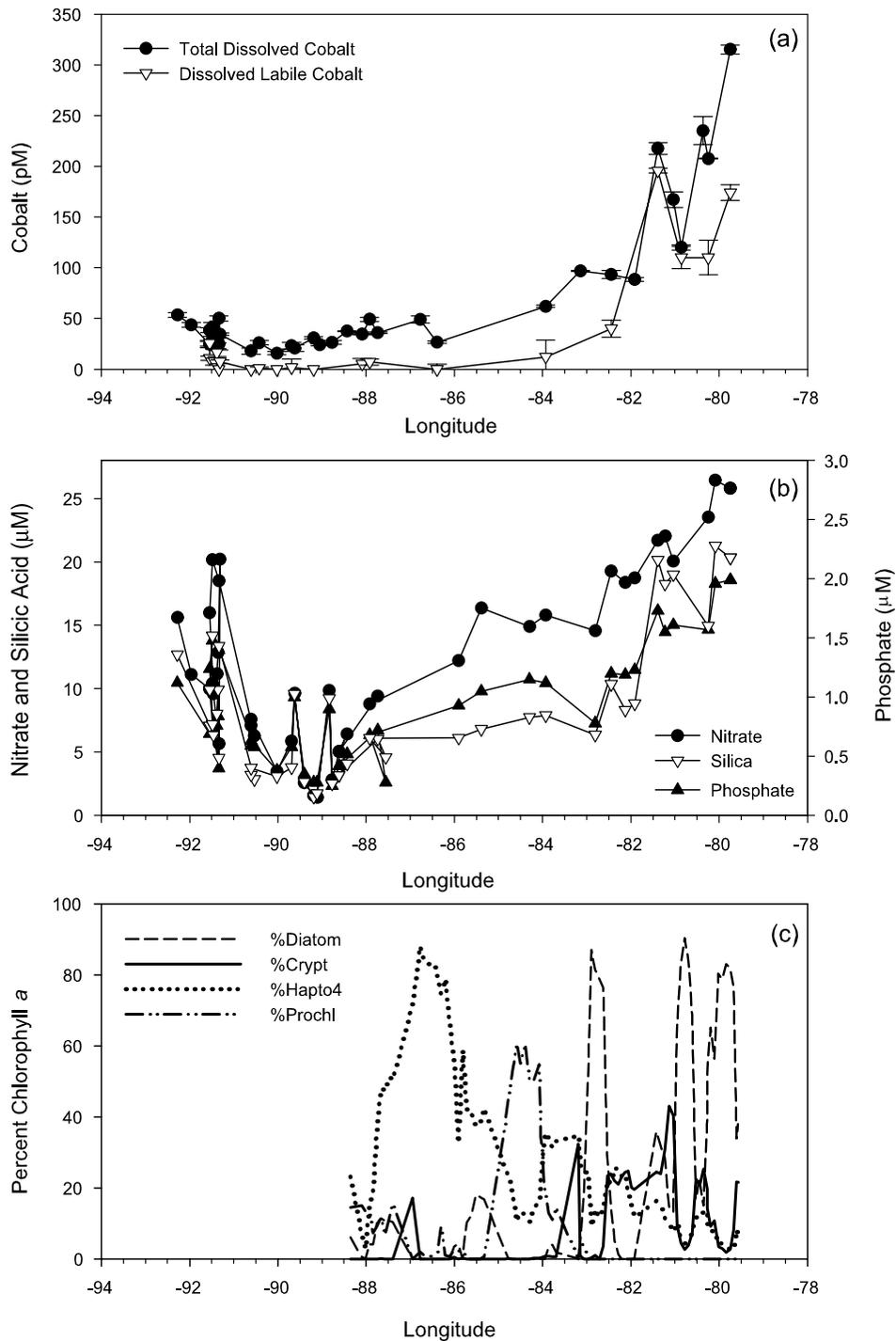
[11] The distribution of major nutrients in seawater is known to be controlled by biological uptake and remineralization [Redfield et al., 1963]. Redfield et al. observed that “[a] number of components of seawater enter into biochemical processes to such a degree that their concentrations are highly variable when compared to the total salinity,” and described a “biochemical circulation as distinct from, though dependent on, the physical circulation of the water.” [Redfield et al., 1963]. While this original analysis was based primarily on seawater nitrate and phosphorus concentrations, it has been observed that the distribution of certain metals such as Zn, Cd, and Cu do not correlate with salinity but rather with other major nutrients like phosphorus [de Baar et al., 1994; Sunda and Huntsman, 1992]. It is not immediately obvious how the biologically utilized trace elements that do not accumulate in deepwaters from remineralization (e.g., the “scavenged-type” elements: Fe, Co, and Mn) should participate in “biochemical circulation.” The distribution and chemical speciation of cobalt in the Peru upwelling region provides important insight into the influence of biochemical circulation on these types of elements.



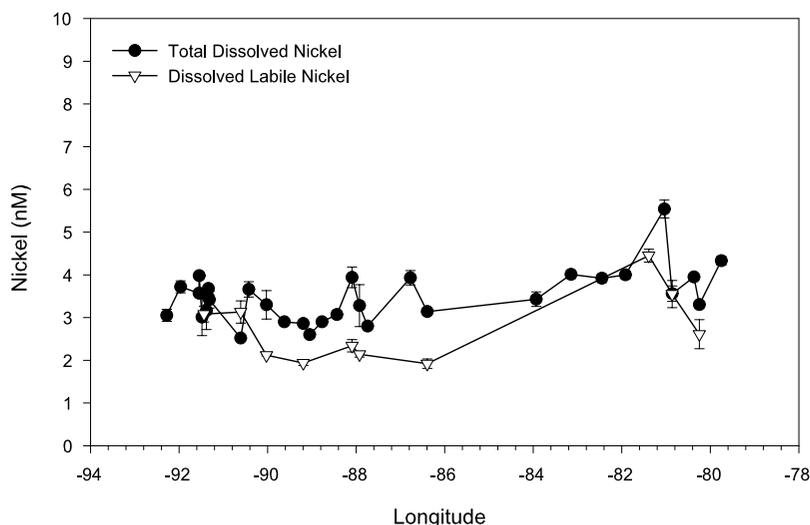
**Figure 2.** (a) Cruise track and stations with cobalt and nickel analyses from the equatorial Pacific to the Peru Upwelling region via the Galapagos Islands, and on a coastal transect in the Peru upwelling region aboard the R/V *Melville* in September 2000. (b) Expanded map of the transect through the Galapagos.

[12] Total dissolved cobalt on the Galapagos-Peru surface transect correlated strongly with orthophosphate and nitrate + nitrite in the upwelling region until cobalt was depleted to  $\sim 50$  pM (Figure 5; nitrate + nitrite, phosphate;  $r^2 = 0.90$ , 0.96). At this point the stoichiometry of cobalt utilization decreased relative to nitrogen and phosphate utilization.

Interestingly, this change occurred where labile cobalt was depleted, leaving only strongly complexed cobalt (Figure 3a). In contrast to previous observations of an inverse correlation between cobalt and salinity in the surface waters of the northwest Atlantic [Saito and Moffett, 2002] (Figure 6 inset) and northwest Pacific [Knauer *et al.*, 1982],



**Figure 3.** (a) Total and labile dissolved cobalt in surface waters on the Galapagos-Peru transect. Between 84° and 91° longitude, cobalt was strongly complexed by organic ligands (as represented by no labile cobalt), reducing the free cobalt concentrations to the femtomolar range. (b) Modest decreases in major nutrients were observed across the transect. (c) The phytoplankton community composition shifted from diatoms to *Prochlorococcus*, and then to the type 4 haptophytes when cobalt became strongly complexed by organic ligands. The type 4 haptophyte group is dominated by *Phaeocystis* species. In polar waters, silicoflagellates and *Parmales* species can also be found within this group.



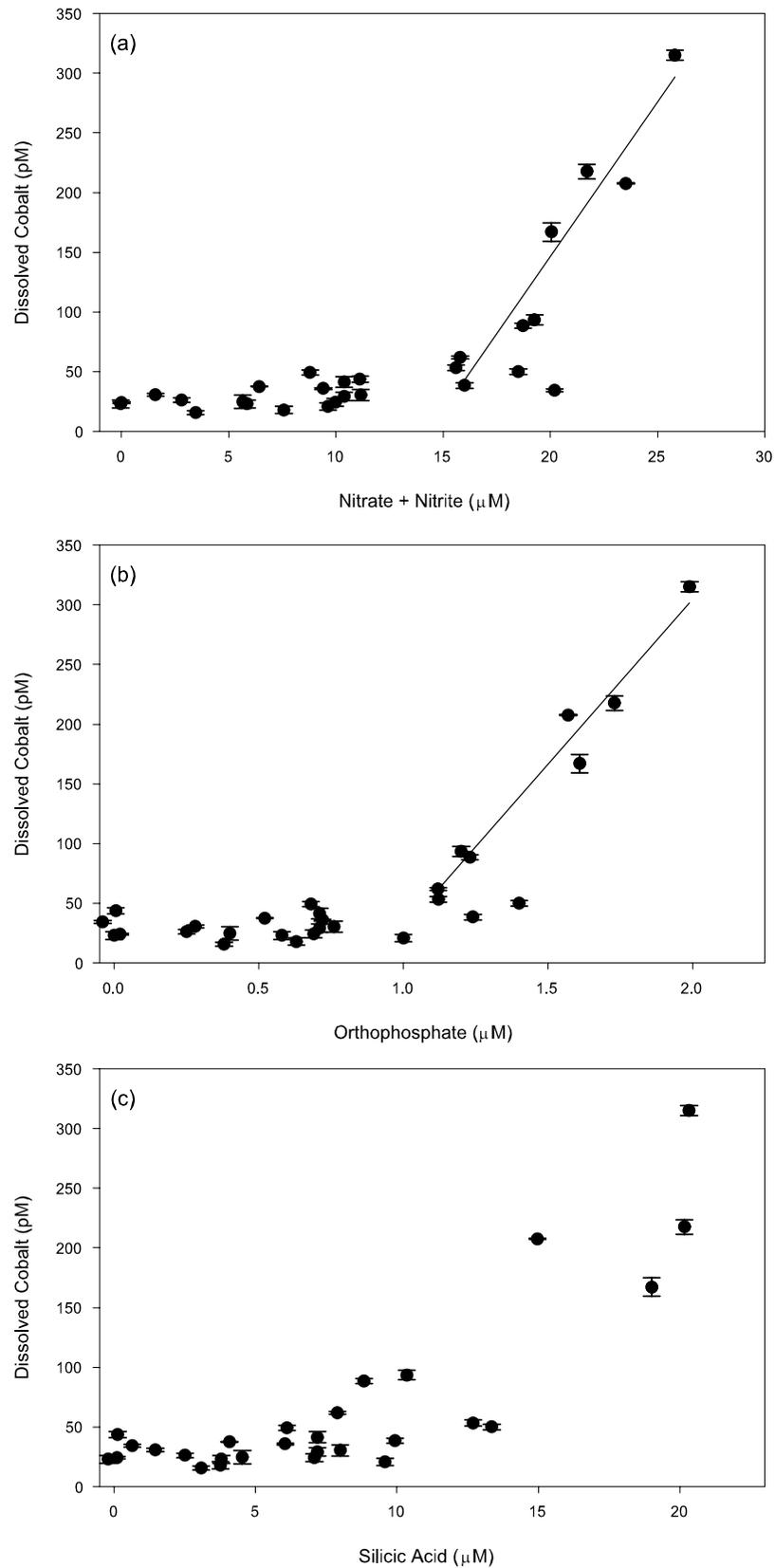
**Figure 4.** Total dissolved nickel and nickel speciation along the Galapagos-Peru transect.

this decrease of cobalt in surface waters was clearly a nonconservative phenomenon with no relationship with salinity (Figure 6).

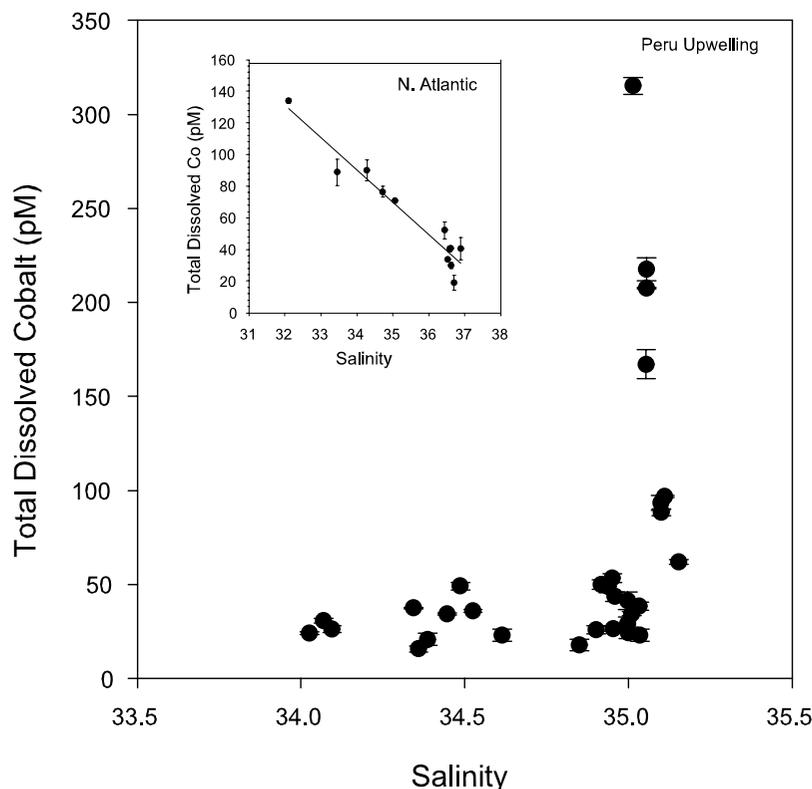
[13] This correlation between cobalt and phosphate in the Peru upwelling region appears to be caused by biological uptake of cobalt, known to be an important micronutrient, and subsequent remineralization. Dissolved cobalt in seawater can be influenced by numerous processes including (1) supply from upwelling (see section 3.4 below), (2) horizontal advection [Martin, 1985], (3) supply from aeolian and riverine inputs [Jickells and Burton., 1988; Saito and Moffett, 2002], (4) removal from surface waters by the biological pump, (5) recycling within surface waters from rapid remineralization of biological material, (6) passive scavenging of cobalt onto particles [Brown and Parks, 2001], and (7) co-oxidation of cobalt by manganese oxidizing bacteria [Moffett and Ho, 1996; Tebo et al., 1984]. Given these multiple forces on steady state seawater cobalt concentrations, the cobalt-phosphate correlation was not initially expected in this region. The presence of a correlation between Co and P but not between Ni and P implies that there is a unique combination of geochemical factors on cobalt controlling its distribution in this environment that is distinct from the geochemical influences on more abundant metals such as nickel. Of the processes listed above, only biological utilization and remineralization processes (items 4 and 5) should be capable of influencing Co and phosphate concentrations simultaneously to create the Co:P correlation observed. While upwelling of intermediate/deepwaters of metals such as Cd, Zn, Ni, and Cu can create a metal:P correlation, this mechanism is not applicable for metals such as Co and Fe because these scavenged metals tend to be low in concentrations in intermediate/deepwaters and hence do not maintain a high Co:P (or Fe:P) ratio or even a consistent ratio in subsurface waters. The lack of a correlation between Ni and phosphate in this region is further evidence that upwelling is not the cause of the metal:P signal since nickel correlates with major nutrients throughout the ocean basins. Alternatively, if there is a localized source of cobalt that is then advected offshore (e.g., from coastal sediments, as

opposed to regional upwelling discussed above), the advection of the water mass with a distinct Co:P signal would cause a correlation between Co and salinity (as we have observed in the Atlantic); no such correlation exists in this region (Figure 6). It is conceivable that the Co:P ratio could be caused by biological remineralization in sediments (see section 3.4) and subsequent upwelling throughout the Peru upwelling region, (versus a localized source with subsequent biological removal in surface waters), yet this seems unlikely since there is likely significant phosphate draw-down (and concomitant Co drawdown) in the surface waters of this highly productive region. Hence the correlation of Co with nutrients in the Peru upwelling region implies that phytoplankton/microbial uptake and remineralization influences the distribution of cobalt more than advective mixing [Saito and Moffett, 2002] or co-oxidation with manganese oxidation [Lee and Tebo, 1994; Moffett and Ho, 1996]. The correlation of cobalt with phosphate observed in this study also suggests that Redfield's biochemical circulation [Redfield et al., 1963] can occur in specific localized regions such as the Peru upwelling region, despite the absence of a conserved ocean-basin wide Co:P ratio. The fact that the chemical speciation of cobalt changes at the transition of where the Co and phosphate correlate (labile cobalt) to where this relationship breaks down (complexed cobalt farther offshore) is remarkable, and implies that the biological utilization of cobalt is strongly influenced by its chemical speciation.

[14] Application of Redfield theory to trace metals has been used to estimate the ratio of metal:P (e.g., Zn:P) in surface water biomass with the assumption that variations in seawater phosphate and metal in the nutricline reflect biological uptake and remineralization [Sunda and Huntsman, 1992, 1995]. A Co:P utilization rate was calculated for the Peru upwelling waters (the slope of the linear regression slope for data greater than  $1 \mu\text{M}$  phosphate in Figure 5b) and is an order of magnitude higher than that of the surface waters of the North Pacific, suggesting higher cobalt cellular quotas in the phytoplankton in this upwelling regime (Table 1). This Co:P value ( $248 \mu\text{mol Co mol}^{-1} \text{P}$ ) is



**Figure 5.** Total dissolved cobalt and major nutrient (nitrate, phosphate, and silicic acid) concentrations correlate until cobalt was at low oceanic concentrations (<50 pM) and strongly bound to organic complexes (see Figure 3a).



**Figure 6.** Total dissolved cobalt in the Peru upwelling waters was rapidly removed relative to changes in salinity, in contrast to northwest Atlantic (inset) where a strong negative correlation with salinity was previously observed [Saito and Moffett, 2002].

comparable to the Zn:P utilization rates in the N. Pacific ( $250\text{--}370\ \mu\text{M Zn mol}^{-1}$ ) [Sunda and Huntsman, 1995] and may indicate a large biological cobalt demand that is not satiated in the open oceans due to cobalt scarcity there. These Co:P values are also on the same order as previous measurements on a transect from equatorial Atlantic to African upwelling waters [Saito and Moffett, 2002], implying that high Co:P utilization may be a characteristic of upwelling waters. In the laboratory, cellular Co:P ratios in the coccolithophore *Emiliania huxleyi*, and the diatoms *Thalassiosira oceanica* and *Thalassiosira pseudonana* can be as high as  $\sim 1000\ \mu\text{mol mol}^{-1}$  P when grown in  $100\ \text{pM Co}^{2+}$  with little indication of saturation or toxicity [Sunda and Huntsman, 1995], while low cobalt concentrations induced growth limitation. The cyanobacteria have an absolute requirement for cobalt that cannot be substituted for by Zn [Saito et al., 2002; Sunda and Huntsman, 1995]. Moreover, the cyanobacterium *Synechococcus* (strain WH8102) appears to be especially sensitive to Cd toxicity [Saito et al., 2003]. Unfortunately, there is no Cd or Zn data from this transect to investigate the possibility of biological

substitution and its manifestation on Co, Cd, and Zn geochemistries. High cadmium has, however, been shown to be a feature of upwelling regimes [Takesue and van Geen, 2002], and hence increased Cd and Zn concentrations likely exist along this transect. Their geochemical sources (and hence their relative magnitude) would differ from that of cobalt, being supplied by mixing from intermediate waters for Cd and Zn or sedimentary fluxes for Co (see below). To our knowledge, neither Zn nor Cd speciation has been measured in upwelling waters, although deepwater Zn and Cd are not complexed as they are in surface waters [Bruland, 1989, 1992; Sakamoto-Arnold et al., 1987], suggesting that upwelled Cd and Zn may also be labile in this environment.

### 3.3. Co and Ni Speciation: Comparison With Phytoplankton Species Composition

[15] The chemical speciation of cobalt has important implications for the bioavailability of cobalt in this region. A dramatic shift in cobalt speciation occurred during the transect with labile cobalt present in freshly

**Table 1.** Relative Surface Water Utilization of Cobalt, Zinc, and Phosphate ( $\mu\text{mol mol}^{-1}$ )

Location	Depth, m	Co, pM	$\Delta\text{Co}/\Delta\text{P}$	Zn, pM	$\Delta\text{Zn}/\Delta\text{P}$
East equatorial Pacific	8	27–315	275	-	-
Northeast Pacific (T5) <sup>a</sup>	50–150	7.9–32	39.8	0.06–0.22	251
Northeast Pacific (T6) <sup>a</sup>	50–150	28–40	35.5	0.14–0.026	370
Northeast Pacific (T8) <sup>a</sup>	8–50	25–55	38.4	0.06–0.32	254

<sup>a</sup>Northeast Pacific data from Martin et al. [1989] and Sunda and Huntsman [1995].

upwelled waters to the east and organic ligand complexes dominating speciation toward the equatorial Pacific. This transition also demarcates a shift from a productive and high export coastal environment to a high internal recycling oceanic environment. These cobalt-ligand complexes were exceedingly strong, as indicated by conditional stability constants in excess of  $10^{16.8}$  [Saito *et al.*, 2004]. The availability of biologically utilized metals in the ocean is thought to be strongly influenced by the chemical form of those metals, where metal uptake rates in phytoplankton cultures are controlled by the abundance of free metal ions present ( $M^{2+}$ ,  $M^{3+}$ ) [Sunda and Guillard, 1976] through a variety of specific metal cation transporters. The ability to utilize organic complexes of iron is thought to be possible in some phytoplankton or bacteria for certain metals under induced conditions, albeit in ways that we are only beginning to understand [Hutchins *et al.*, 1999]. However, chemical speciation measurements have shown that many transition elements in seawater exist predominantly as metal-organic ligand complexes with exceptionally strong conditional stability constants. Determining the chemical structures of the organic ligands in natural seawater remains a formidable analytical challenge [Macrellis *et al.*, 2001], and it has been hypothesized that some of these ligands may be produced by microbes and that they can be utilized directly in their metal-organic ligand form (e.g., siderophores and cobalophores) [Rue and Bruland, 1997; Saito *et al.*, 2002; Wilhelm *et al.*, 1998].

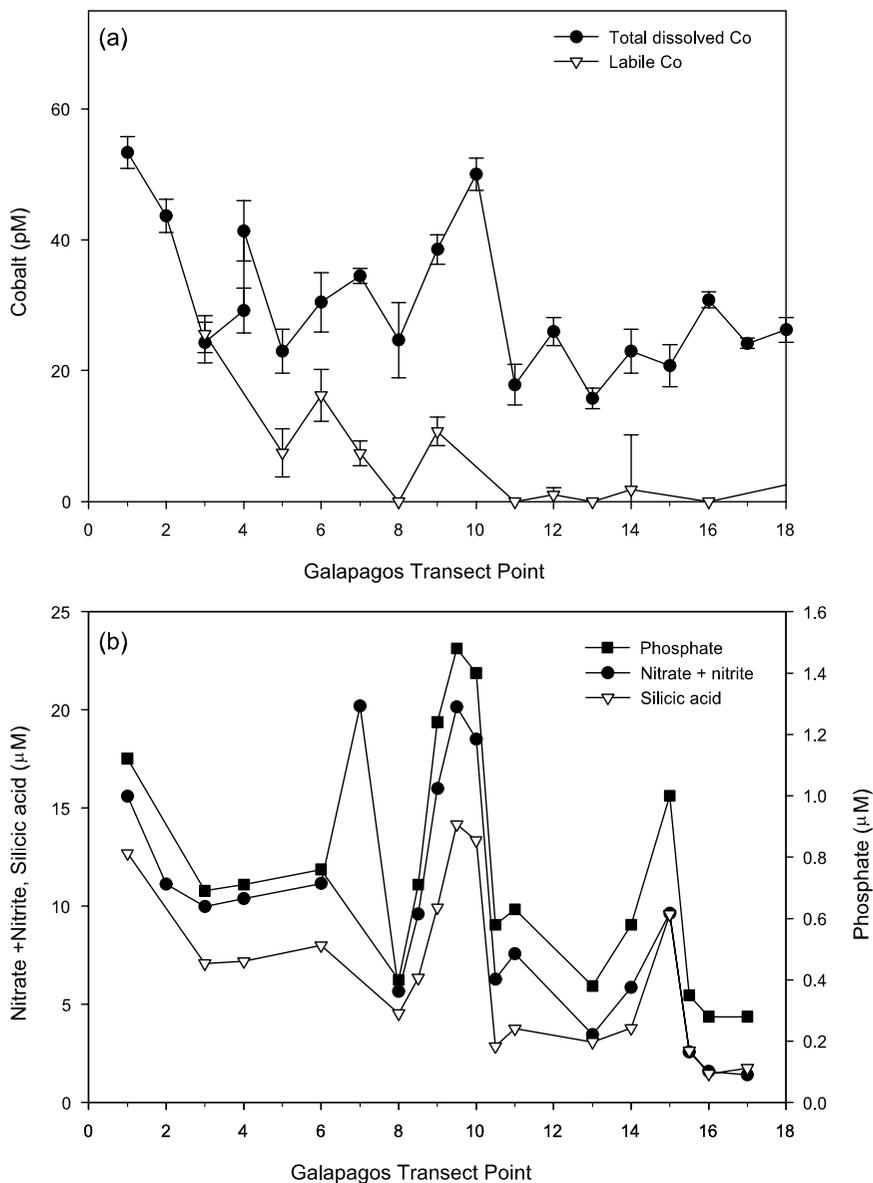
[16] The change in the chemical form of cobalt along this transect due to upwelling of labile cobalt may have an important effect on phytoplankton species composition, favoring those species that can grow faster but lack the ability to acquire complexed cobalt in the upwelling region, while favoring organisms that can utilize complexed cobalt in the oceanic regions. The Co:P utilization ratio is consistent with this idea, showing significantly less utilization of Co relative to phosphate once Co is bound by strong organic ligands (Figures 3a and 5b). HPLC pigment data are also consistent with this idea: The phytoplankton community composition shifts from being dominated by diatoms, then *Prochlorococcus*, followed by *Phaeocystis*, as cobalt is depleted and its chemical speciation changes from labile to strongly complexed (Figure 3c). This speciation change corresponds to a decrease in free cobalt concentration ( $Co^{2+}$ ) from  $\sim 300$  pM to fM or lower concentrations ( $>4$  orders of magnitude) when the high conditional stability constant of cobalt ligands is taken into account [Ellwood and van den Berg, 2001; Saito and Moffett, 2001]. In comparison, major nutrients remain at high concentrations (e.g.,  $NO_3^- > 4$   $\mu M$ ) across this gradient (except near the Galapagos islands). While surface waters in this region have been observed to be Fe limited [Hutchins *et al.*, 2002], the dynamic range of  $Co^{2+}$  observed here is clearly large enough to influence the community composition of phytoplankton populations. These results are consistent with observations of both  $Co^{2+}$  and organically complexed cobalt use by the cyanobacterium *Prochlorococcus* [Saito *et al.*, 2002], and suggest that *Phaeocystis* has the ability to either access organically complexed cobalt or substitute another metal for it.

[17] In contrast to cobalt, nickel speciation measurements show labile nickel present throughout the transect. While this is not surprising, considering that the total nickel does not change significantly throughout the transect, it does shed light on questions raised in an earlier study about the possibility of cobalt and nickel competing for the same ligand sites and the redox state of cobalt when bound to natural ligands [Saito and Moffett, 2001]. The presence of labile nickel when there is effectively no labile cobalt in the middle portion of the transect suggests three possibilities: (1) The ligands for cobalt and nickel are distinct and do not compete for both metals, (2) if there is a set of ligands that can bind both metals, they bind cobalt over nickel preferentially, or (3) there are cobalt ligands which bind cobalt very strongly, likely in the Co(III) oxidation state, with which the ligands that bind nickel cannot compete. The second possibility seems unlikely if cobalt is in the +2 oxidation state, given that the synthetic ligands in the NIST database that have high cobalt affinities tend to have higher nickel affinities [Martell and Smith, 1993; Saito and Moffett, 2001]. Possibilities 1 and 3 above are not necessarily mutually exclusive, since it is well known that organic Co(III)-ligands bind cobalt extremely strongly and have very slow dissociation kinetics [Shriver *et al.*, 1990]. In concurrent studies, the strength of ligands in the Costa Rica Upwelling Dome revealed cobalt ligands to be exceedingly strong, with a log  $K$  of  $>16.8$ , supporting the third possibility of a Co(III) organic ligand existing in nature [Saito *et al.*, 2004].

### 3.4. Evidence for a Sedimentary Cobalt Flux

[18] The Peru surface water cobalt concentrations presented here likely originate as a flux from anoxic sediments, and this flux of cobalt may constitute a major source of cobalt to the coastal Peru ecosystem and perhaps to the surface waters of the South Pacific. The potential for cobalt release from sediments has been experimentally validated: Studies of cobalt in pore waters have indicated that cobalt is recycled with manganese between oxic and suboxic sediments [Heggie and Lewis, 1984]. When bottom water  $O_2$  is sufficiently low, as in the Peru upwelling region [Friederich and Codispoti, 1987], microbial oxidation of upward diffusing reduced Mn at the sediment water interface does not occur and Mn can be released to the water column [Thamdrup *et al.*, 1994]. Benthic flux chamber measurements have shown that suboxic sediments can be a source of dissolved cobalt to bottom waters [Sundby *et al.*, 1986], presumably by release of Co associated with manganese oxides. The influence of sedimentary sources on the water column distribution of cobalt has also been shown: Sedimentary sources can create elevated concentrations of cobalt in low oxygen bottom waters ( $\sim 124$  pM at 879 m depth) of the Santa Monica basin; however, this dissolved cobalt was scavenged to 30 pM by 500 pM depth and hence this source did not appear to supply the Santa Monica surface waters [Johnson *et al.*, 1988].

[19] In the Peru upwelling waters, the cobalt that is associated with upwelling appears to dominate over other input sources. A simple estimate of a flux of  $19.9 \times 10^6$  mol  $yr^{-1}$  Co in the Peru upwelling waters is large

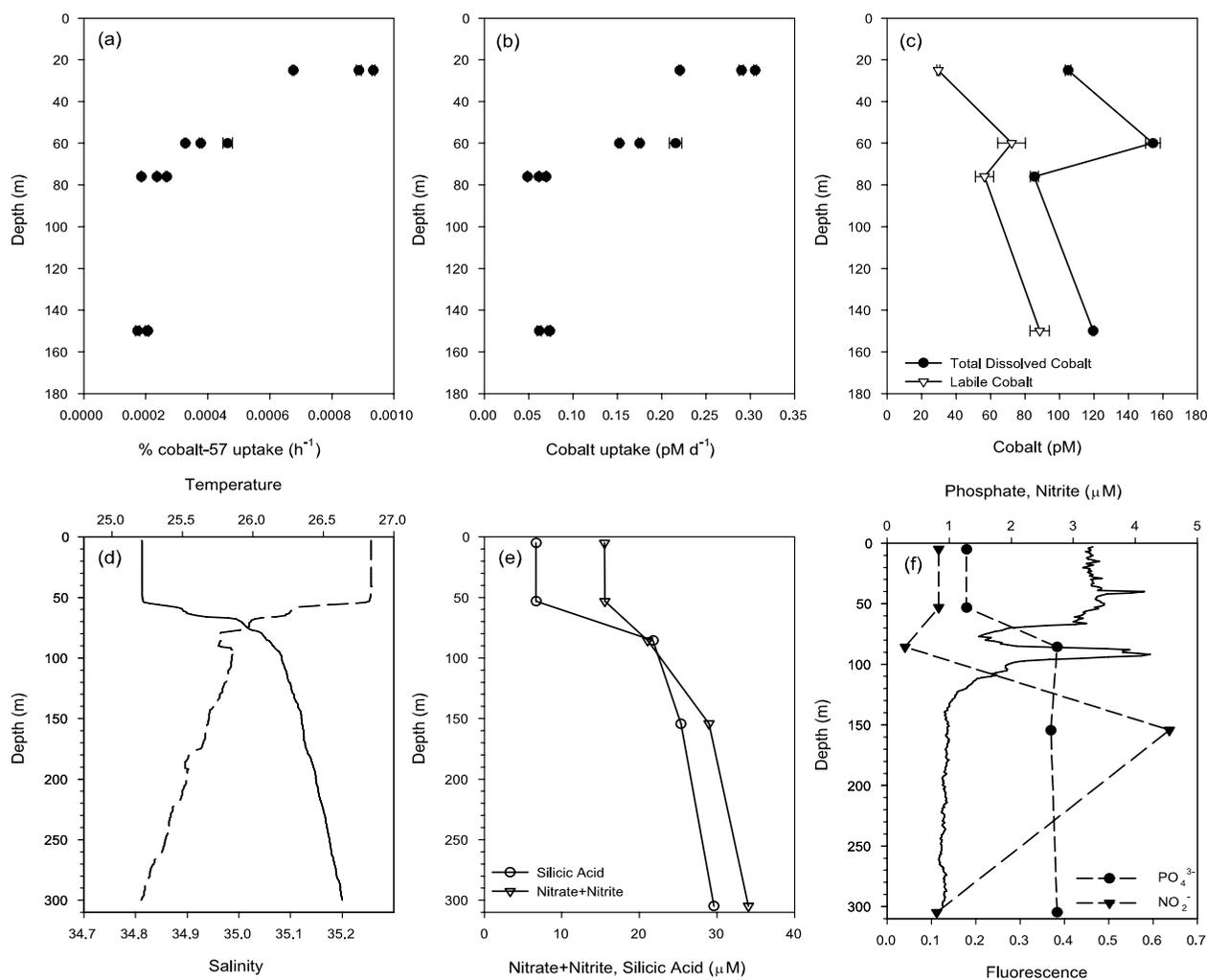


**Figure 7.** (a) Island effects on total dissolved cobalt and cobalt speciation in the Galapagos Islands. (b) Major nutrient concentrations. Transect points relate to station numbers plotted in Figure 2b.

enough to replenish 11% of the cobalt in the entire surface Pacific Ocean (300 pM surface water Co entrained in the estimated upwelling volume in the Peru upwelling system [Figueroa and Moffat, 2000]; estimated Pacific inventory is based on a 50-m mixed layer with 20 pM Co). The presence of a high nitrate surface water tongue from Peru and low  $\Delta^{14}\text{C}$  values in Pacific corals south of the equator show that Peru upwelling waters originate from the Equatorial Undercurrent and can travel west across the surface of the entire Pacific basin [Toggweiler and Dixon, 1991] and hence could deliver entrained cobalt to the surface Pacific. However, it should be pointed out that based on the limited data set and lack of profile data in this region, it is unclear the extent to which the upwelled cobalt is recycled within surface and subsurface waters versus how much escapes

associated with particles and is returned to the sediments. While this flux calculation is clearly simplistic and should be revisited with a more comprehensive model and additional data, it nevertheless serves as a useful vehicle for outlining the potential geochemical importance of this feature.

[20] The high concentrations of cobalt measured here do not appear to be supplied by resuspension of sediments, as Johnson *et al.* [1999] have shown for iron in the California coastal system. Our analytical procedure contrasts that of Johnson *et al.* in that our samples were 0.4  $\mu\text{m}$  filtered (versus 10  $\mu\text{m}$ ) and were not acidified during analysis. Sediments would have been filtered out with this smaller filtration pore size, and the analysis of fresh ambient pH samples would not induce the release of metals from the



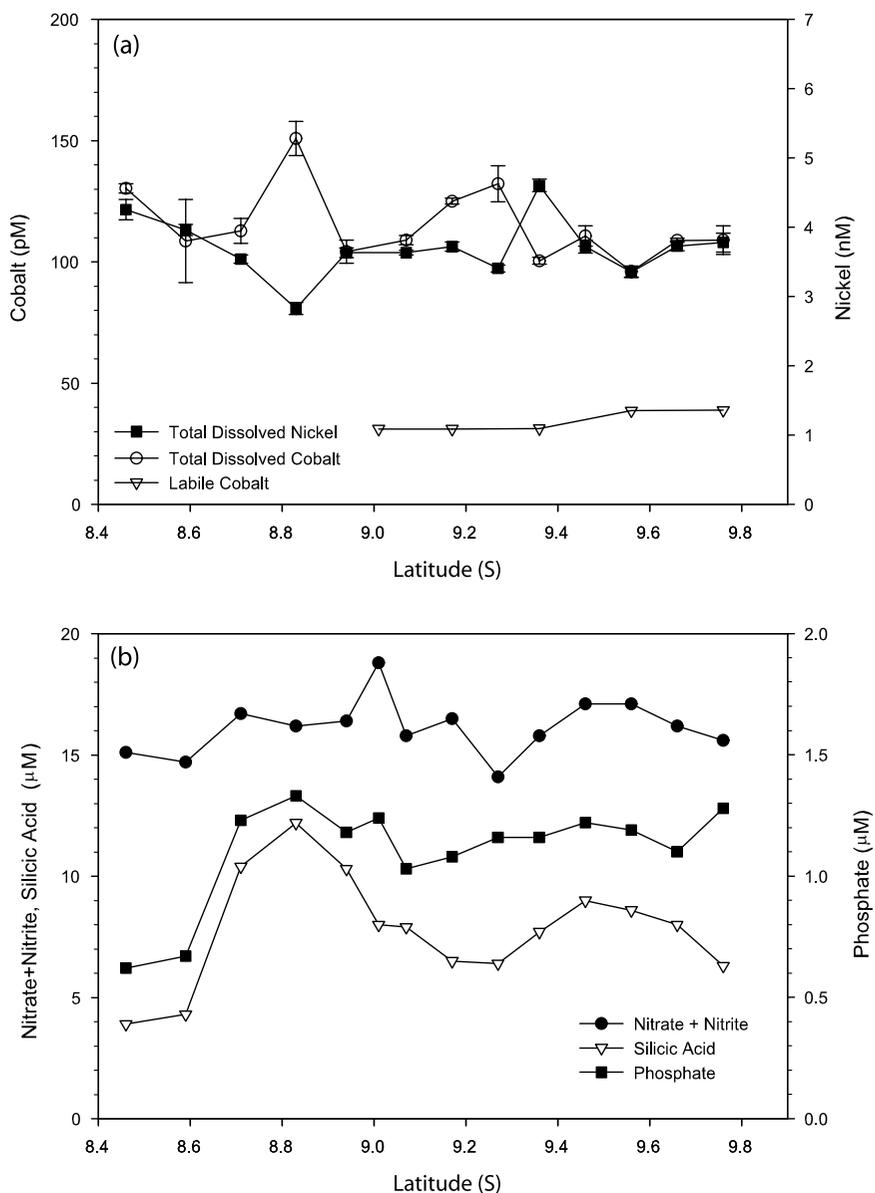
**Figure 8.** (a) Cobalt uptake rates as percent of total tracer, (b) cobalt uptake rates in  $\text{pM d}^{-1}$ , and (c) total dissolved cobalt and cobalt speciation on a vertical profile in the Peru upwelling region at  $9.8^{\circ}\text{S}$ ,  $81.6^{\circ}\text{W}$ . Hydrographic data at this site: (d) salinity (solid line) and temperature (dashed line); (e) nitrate + nitrite and silicic acid; and (f) CTD fluorescence (solid line), nitrite, and phosphate.

particulate material as with the acid leach step involved in the iron analysis. In a separate study, cobalt in the bottom waters of the Santa Monica basin were analyzed with  $0.45 \mu\text{m}$  filtration and without acidification [Johnson *et al.*, 1988], and showed elevated bottom water concentrations, consistent with our results. While both Fe and Co may have significant sedimentary fluxes in these coastal environments, their mechanisms of release appear to be distinct.

### 3.5. Island Effects

[21] A previous study examined the influence of island-induced upwelling of the Equatorial Undercurrent around the Galapagos Islands, showing slightly enhanced concentrations of iron, nickel, zinc, and cobalt around the islands [Gordon *et al.*, 1998]. The surface transect presented here has somewhat higher sampling resolution through the islands, especially near the largest, Isabella (Figure 2b). The lower values in this study are similar to those of Gordon *et al.*, and the higher sampling resolution in this

study reveals cobalt and associated nutrient peaks that are several-fold higher than the rest of the transect (Figure 7). The highest concentrations were observed west of the islands (stations 1 and 2) and just south of Isabella island (stations 9 and 10). Southern Isabella contains the active volcano Cerra Azul, and has a bathymetry that drops off sharply to more than 2000 m immediately south of the island. The higher cobalt concentrations seem indicative of upwelling given the concurrent increased major nutrient concentrations, rather than dust or volcanic associated inputs. No major changes in cobalt concentrations are observed close to San Cristobal (stations 14 and 15) and Santa Cruz islands (stations 11 and 12), and this is likely related to the somewhat shallower waters and increased distances from steep bathymetric features. Volcanic rocks contain comparable cobalt concentrations as continental crust (19 ppm, 25 ppm, and 25 ppm for Canadian Shield, Northwest Scottish Highlands, and Andesitic volcanic model [Taylor and McLennan, 1985]), and enhanced seawater



**Figure 9.** (a) Total dissolved cobalt and nickel, and cobalt speciation on the southern surface transect in the Peru upwelling region. (b) Major nutrients on the transect.

cobalt concentrations may be dependent on episodic erosion events.

### 3.6. Cobalt Uptake Studies and Southern Surface Transect

[22] Previous studies have found that cobalt uptake is dominated by its microbial co-oxidation with manganese in coastal waters, such as Vineyard Sound, Massachusetts, and in fjords [Moffett and Ho, 1996; Tebo *et al.*, 1984], while in oligotrophic environments like the Sargasso Sea, phytoplankton uptake is the dominant removal mechanism for cobalt [Moffett and Ho, 1996]. Direct measurements of cobalt uptake rates were made using radiotracer addition incubation experiments on a vertical profile within the Peru upwelling region (Figure 8). Vertical and horizontal distributions of cobalt were also determined in this location, with

uptake experiments performed at the end of the southern transect (Figures 9 and 2a). This transect ended prior to returning to oligotrophic waters, and hence little variation was observed in total dissolved cobalt, nickel, or major nutrients in the surface waters. Moreover, cobalt speciation showed significant concentrations of labile cobalt at the end of the transect (Figure 9) and in the vertical profile (Figure 8c).

[23] Cobalt uptake rates increased approximately fivefold in surface waters (Figures 8a and 8b) relative to 76 and 150 m depths, likely due to the enhanced photosynthetic activity in the mixed layer (Figure 8f). The low cobalt uptake rate at 76 m is just above what is believed to be a deep *Prochlorococcus* suboxic maxima (Figure 8f), and may be low owing to slow growth and grazing of that population. As noted above, the major removal mechanism

of cobalt in previously studied coastal waters is microbial co-oxidation with Mn oxides. While Mn oxide formation was not measured in this experiment, Mn oxides are known to undergo photodissolution via sunlight induced H<sub>2</sub>O<sub>2</sub> production in surface waters [Sunda and Huntsman, 1994; Sunda et al., 1983], and hence the enhanced cobalt uptake in surface waters is not consistent with expected vertical Mn oxidation activity. Furthermore, evidence of Mn oxidation in the eastern equatorial Pacific has not been observed in surface waters or in the oxygen minimum zone [Cowen and Bruland, 1985; Moffett, 1997]. On the basis of these previous studies, the higher cobalt uptake rates in surface waters are consistent with its removal as a micronutrient via phytoplankton uptake and rather than Mn oxide formation in this environment, and are consistent with the nutrient-like vertical distribution of dissolved cobalt (Figure 8c). Hence, unlike previously studied coastal environments, cobalt uptake associated with the high primary productivity of the Peru upwelling must be significant enough to overshadow cobalt co-oxidation with Mn oxide production.

### 3.7. Implications and Conclusions

[24] The large flux of labile cobalt in upwelled waters, its rapid removal as a micronutrient, and the role of cobalt speciation on cobalt utilization have important implications for our understanding of the biogeochemistry of cobalt. The major sources of cobalt to the oceans have not been rigorously documented. For trace elements like Fe and Co that lack significant deepwater inventories, adequate supply to the surface ocean for phytoplankton demand could easily become problematic. Riverine input, aeolian deposition, hydrothermal input, and sedimentary sources are all likely contributing to the geochemical cycling of cobalt. A previous time series study in the Sargasso Sea did not show significant evidence of dust deposition [Saito and Moffett, 2002]. Moreover, the Co:Fe ratio in crustal matter is 1:2600, implying that dust deposition is less important for cobalt than iron [Duce et al., 1991; Taylor and McLennan, 1985]. In comparison, the microbial reduction of cobalt oxides associated with Mn oxides in sediments with low oxygen bottom waters could be a major input of cobalt to the surface ocean. The presence of this cobalt in a labile form implies that chemical speciation measurements could be used as a signature of “new” cobalt derived from sedimentary sources, as opposed to recycled cobalt that circulates through the surface and deep oceans and appears to be very strongly bound through its interaction with the biota. Finally, this is the first data set documenting a large change in metal lability concurrent with large changes in the phytoplankton assemblage suggestive of the importance of speciation on the phytoplankton community composition.

[25] Physical processes such as El Niño events may play an important role in reducing the flux of cobalt to these upwelling areas and beyond to the open ocean. With decreases in wind-induced upwelling associated with the El Niño phenomenon, less cobalt enriched bottom water would be brought to the surface. In addition, the decrease in productivity associated with El Niño events might also allow oxygen concentrations to increase in bottom waters,

allowing manganese oxidizers in the surface sediments to coprecipitate cobalt before it diffuses out of sediments, and hence reducing bottom water cobalt concentrations. As a result, the occurrences of El Niño events may have important implications for interrupting the marine biogeochemical cycle of cobalt by decreasing the surface water inventories of cobalt with potential changes in the phytoplankton community structure and biological carbon pump.

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G. R. DiTullio, Grice Marine Laboratory, Department of Biology, College of Charleston, 205 Fort Johnson, Charleston, SC 29412, USA. (ditullioj@cofc.edu)

J. W. Moffett and M. A. Saito (corresponding author), Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA. (jmoffett@whoi.edu; mak@whoi.edu)