

Interactive comment on “A seasonal study of dissolved cobalt in the Ross Sea, Antarctica: micronutrient behavior, absence of scavenging, and relationships with Zn, Cd, and P” by M. A. Saito et al.

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We are very appreciative of the effort expended by the reviewers in carefully reading and commenting on the manuscript. We are also quite appreciative of the kind words regarding the quality of the manuscript from all three reviewers. In this Author Comment we provide responses to the reviewers' comments.

Reviewer #1:

We thank the reviewer for the kind words about our data quality and manuscript's con-

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tribution to Southern Ocean research.

The reviewer suggested a number of more recent papers on metal-phytoplankton quotas. We agree that those papers also provide insight into metal quotas, and we will include appropriate references. However, we feel that the Sunda and Huntsman manuscripts are more valuable because they are conducted under zinc and cobalt limiting conditions, while the suggested references of laboratory quota studies were conducted at non-limiting concentration of metals. As a result, the values in the suggested manuscripts are less realistic, not reflective of biochemical requirements, and hence not suitable for comparison to our field measured ecological stoichiometries. Moreover, in the studies by Sunda and Huntsman, great care was taken to examine the influence of Co quota in response to Zn availability, and vice versa. This is critically important for our application of comparing our field estimates of Zn and Co ecological stoichiometries with values that have been shown to be limiting. If invited to revise the manuscript for Biogeosciences, we will take these comments (including the interesting last comment) into consideration in the revisions.

Zn speciation references: We thank the reviewer for pointing out these new references. These results are consistent with our findings here and will be useful in citing for the purposes of our discussion.

We thank the reviewer for pointing out these additional Southern Ocean trace metal references, which will be included if applicable in the potential revised version. The North Pacific dataset of Martin et al is a particularly high-quality dataset for all of these metals simultaneously, and is also particularly relevant because it has been used previously by Sunda and Huntsman for their meta-analyses. It also provides a useful contrast to this study's Southern Ocean geographic study. We agree entirely that a comprehensive comparison should be made of all of these study sites (including some assessment of data quality), yet such a project is beyond the capabilities for our analysis and discussion here.

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We agree with the uncertainties regarding the analytical methods for Martin et al dataset from the North Pacific. We brought attention to this need for UV irradiation of total cobalt samples during the GEOTRACES intercalibration process, and are pleased that this issue has been recognized in the GEOTRACES intercalibration documents. We agree that this is an issue that needs to be examined with respect to historical datasets, hopefully in these ongoing GEOTRACES intercalibration studies. Yet that particular dataset of Martin et al. appears to have far better precision for cobalt than most other historical studies (including the Fitzwater dataset from the Ross Sea we discuss), as observed in the very clean relationships observed with phosphate, which is relatively unusual in cobalt datasets in the literature. Also, our unpublished results from the North Pacific have found that cobalt is quite labile there, which might contribute to the coherence between the dithiocarbamate method and phosphate abundances. We currently have a very brief qualification in the manuscript regarding this specific point, but in a revised manuscript we could add a little more substance to this qualification and uncertainties if appropriate.

Particulate Co data: We do not have nor know of any particulate metal data that are published, but we do know of other studies that are underway. Hopefully in the future we will see more coupled dissolved and particulate metal studies.

Scavenging: We thank the reviewer for pointing out this references, and will include a discussion of this point in a revised manuscript.

B12 lability: We will include some discussion regarding the lability and binding strength of B12. In particular, by our labile method B12 is not detected and the cobalt does not dissociate from B12 to any detectable degree, consistent with the comments by this reviewer. We agree with the reasoning of B12 complexes (and degradation products) and the difficulties of examining historical data. Fortunately, there isn't very much historical data for cobalt.

Shorten section 3.4: In a revised version this section will be shortened. However, as we

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were writing this section, it became clear to us that there is a great deal to be discussed regarding this topic, including material with relevance to our interpretation of the Cd:P relationship in seawater. One reason we chose BG was because of the lack of page limits that allow this type of in-depth discussion.

0.4 μm filtration and archaea: This is a good point and what that needs to be addressed throughout trace metal oceanography since the filters of choice have until recently been 0.4 micron.

Equilibration time of radiotracer with seawater: This is a very good point. We made the equilibrated stock once for each cruise and used it throughout for uniformity, storing it at 4C in darkness. This approach should allow the radiotracer to equilibrate with any weak Co ligands present that would be measured as part of the total but not the labile fraction. As the reviewer points out, it is very unlikely that the equilibration occurs with the strong complexes. Ideally, the uptake measurements should be normalized to some intermediate value between total and labile representing this fraction of complexes with which equilibration was reached. Since this is not possible, we chose to normalize to total uptake rates. This is also in part a practical decision since at many points in the surface waters where these rates were measured, labile cobalt was not measured. If labile Co concentrations are used to make the calculation of uptake rates where they were above the detection limit, the trends are largely the same as when the Co total measurements are used. In a potential revised manuscript, a discussion of which Co measurement is most appropriate could be included.

Uptake rate time course: We do have data for a 24 hour timecourse suggesting that tracer uptake over this time is constant and roughly linear ($r^2 = 0.986$) over 24 hours, supporting our use of this linear relationship to calculate uptake rates. We would discuss or present (if space allows) this data in a potential revised version and discuss its implications. Also, since we add tracer-level amounts of Co, this should not change the overall concentration of Co, so that we do not need to worry about concentration dependency of the uptake rate in this calculation. It is difficult to resolve how the rate

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dependency changes as a function of Co concentration during this timecourse experiment since the percent uptake in this case remains less than 2% over the 24 hours and deviations from a linear trend may be difficult to resolve. Prolonging this measurement to increase Co drawdown would have meant significant community composition changes in a bottle incubation making the measurements difficult to interpret, so we did not conduct these experiments.

Unlikely there is diffusion limitation of Zn given that there is labile Zn: We politely disagree. Our stoichiometric comparisons show that the values present in the Ross Sea are actually already below the Zn:P needs of coastal diatoms. Moreover, the Ross Sea is home to very intense blooms that do create significant drawdown of nutrients and CO₂ in some specific geographical areas (as low as ~100ppm). It seems possible that such low CO₂ high productivity conditions could create zinc depletion that could well be carbon-zinc co-limited in the Ross Sea.

Reviewer #2 M. Ellwood

This review appears to be truncated. We will respond as best possible under these circumstances. We appreciate the comment that the data appear to be of high quality. We politely disagree with the notion that the ecological stoichiometry section is not particularly relevant. One of the failings of modern trace metal oceanography is our inability to compare elements. Too often manuscripts on one metal fail to compare and contrast the geochemical observations with those of other metals, often to the detriment of our knowledge of both (this reviewer is one of the few that does make such multi-element studies). Moreover, we feel that the linkages to Zn and Cd here are particularly important given the capability for biochemical substitution in the phytoplankton that dominate this region (most diatoms and *Phaeocystis antarctica* have Zn-Co substitution capability). Finally, this comparative approach allows us to gain insight into and provide an alternative explanation for the Cd:P kink. We will consider AOU and preformed phosphate relationships in a revised manuscript.

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Reviewer #3

We appreciate the reviewer's kind words about the data quality and manuscript. Regarding the confusion with the biological requirements for Co, it is true that cobalt has these two roles of cambialistic enzymes and vitamin B12, the latter of which must pass through prokaryotes in order to be made into the B12 form, since no known eukaryotic phytoplankter (or eukaryote at all) can make B12. In revisions we will look to improve clarity of the manuscript regarding these points.

In a revised version we will add further discussion of the physical oceanographic properties of the study site.

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