

Review of MS “New insights on the role of organic speciation in the biogeochemical cycle of dissolved cobalt in the southeastern Atlantic and the Southern Ocean” by J. Bown, M. Boye, and D. M. Nelson.

This manuscript presents new cobalt speciation data for the south Atlantic region of the Southern Ocean. The dissolved cobalt data appears to be of a high quality. However I have concerns regarding the ligand titration data. My major concern is with the rather high conditional stability constants ( $K'_{CoL}$ ) (see section 4.2.1) obtained in this study for the cobalt-ligand complex relative to the earlier work of Ellwood and van den Berg 2001, Ellwood et al 2005 and Saito and Moffett 2001. In these earlier studies  $K'_{CoL}$  obtained for the cobalt-ligand complex range between  $10^{15}$  to  $10^{17}$ ; whereas in this study  $K'_{CoL}$  values range between  $10^{17.9}$  to  $10^{20.3}$  – 1 to 5 orders of magnitude great than previous work. Brown et al suggest that this difference is related differences in the detection window used between studies. However, it appears to me that these relate to differences in the pH used in each study. pH has a strong influence on the formation constant ( $\beta'_{CoNioxime2}$ ) for the cobalt-nioxime complex and well as the cobalt-DMG complex (another ligand used in determining cobalt speciation) (see table below).

pH	$\log \beta'_{CoNioxime2}$	$\log \beta'_{DMG}$
8		11.5 <sup>@</sup>
8.7	15.6 <sup>%</sup>	12.8 <sup>%</sup>
9.1	18.1 <sup>#</sup>	

<sup>%</sup> Data taken from Zhang et al 1990

<sup>@</sup> Data taken from Saito and Moffett 2001

<sup>#</sup> Data taken from Ellwood and van den Berg 2001

Brown et al have use Zhang et als value of the  $\beta'_{CoNioxime2}$  for the cobalt-nioxime complex of  $10^{15.6}$ , which was calibrated at a pH of 8.7 (see Ellwood and van den Berg 2001 for discussion). However, Brown et als titrations were undertaken at a pH of 8.1. Based on the pH sensitivity of the cobalt-nioxime and hence  $\beta'_{CoNioxime2}$ , it is likely that this value of  $10^{15.6}$  is too high making it inappropriate for use at this pH (8.1). Thus all of Brown et als  $K'_{CoL}$  values for the cobalt-ligand for field data will also be too high, which is observed when their titration data are compared to other studies from the south Atlantic region.

To correct this issue the  $\beta'_{CoNioxime2}$  for the cobalt-nioxime needs to recalibrated against EDTA to a pH of 8.1 . Once this is done all Brown et als titration data can then be corrected. If this is not done then the ligand data present in this study, and some of the discussion and conclusions reached in this manuscript, are meaningless along with estimates for inorganic cobalt concentration.

I recommend that the manuscript be rejected unless the  $\beta'_{CoNioxime2}$  for the cobalt-nioxime complex is recalibrated to a pH of 8.1.