

On the nature of dissolved copper ligands in the early mixing zone of hydrothermal vents

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Hydrothermally sourced copper (Cu) has been recognized to be partly stabilized against precipitation by its complexation with strong Cu-chelates [1]. However, the source and nature of these compounds in such environments are still poorly documented. Here we investigated the apparent speciation of Cu from the early mixing with seawater of two black smokers (Aisics and Y3) at the hydrothermal vent field Lucky Strike (Mid-Atlantic Ridge) using competitive Ligand Exchange – Adsorptive Cathodic Stripping Voltammetry (CLE – AdCSV) [2]. We have assessed the Cu binding ligands concentration ([L]) and the corresponding conditional stability constant (Log K') for 24 samples. At the smoker Aisics, [L] values ranged from 18.2 to 1060 nM. Log K' ranged from 12.4 to 13.4. At Y3, the binding capacity of natural chelates was from 32.5 to 1020 nM, with Log K' ranging from 12.5 to 13.1. Total dissolved Cu ranged from 2.19 to 770 nM and from 12.7 to 409 nM at Aisics and Y3, respectively. Our results show that the amount of ligand L increases with dissolved Mn (dMn) concentrations, suggesting a hydrothermal origin of the Cu-chelates detected. By plotting [L] against *in situ* total dissolvable sulfides ($\Sigma S = H_2S + HS^- + S^{2-}$) measured by the CHEMINI analyzer [3], a positive statistically significant correlation was found at Y3 ($p < 0.05$; $r^2 = 0.87$). At Aisics, [L] are following the trend of ΣS when plotting both parameters against dMn. We thus infer that Cu binding ligands could be predominantly inorganic sulfur species in the studied area.

[1] Sander *et al.* (2007) *Env. Chem.* **4**(2), 81-89.
[2] Campos & van den Berg (1994) *Anal. Chim. Acta.* **284**(3), 481-496. [3] Vuillemin (2009) *Deep-Sea Res. I* **56**(8), 1391-1399.