Evidence for organic complexation of copper in deep-sea hydrothermal vent systems

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Deep-sea hydrothermal vents represent a natural habitat for many extremophile organisms able to cope with high temperature and pressure, and unusual chemical gradients such as high concentrations of heavy-metals. The complexation of copper and other heavy-metals with free-inorganic sulfides in hydrothermal waters is considered to dominate their chemical speciation and bioavailability [1]. However, it is now well established that in the ocean at large, the biological availability of all essential or toxic metal ions are controlled by the formation of strong complexes with natural organic matter ligands of which many are presumed to be of biological origin, produced either to acquire metal-ions (e.g. Fe^{3+}) or to reduce their toxicity (e.g. Cu^{2+}).

For the first time we have demonstrated that organic complexation also plays an important role in the chemical speciation of copper, and probably other heavy-metals, in hydrothermal vents and in their mixing zone with seawater. In samples from deep-sea hydrothermal vents from the Kermadec-Arc, Pacific and the Logatchev-field, Mid-Atlantic-Ridge we found very high concentrations of strong organic copper-binding ligands, up to 4 µM with conditional stability constants between $\log K''_{CuL,Cu2+} = 12.48$ and 13.39. These values are very high compared to those observed in most deep-seawaters and the resulting Cu-binding capacity high enough to play an important role in controlling the bioavailability and geochemical behaviour of metal-ions around hydrothermal vents.

Our measurements were made using competing-ligand-equilibration cathodic-stripping-voltammetry, at ambient seawater pH to mimic the conditions in the hydrothermal fluid/seawater mixing-zone, and, where necessary, after removal of acid volatile sulfides and diluting the samples with artificial seawater. The significance of organic ligands in comparison to sulfide is discussed. Further voltammetric investigations indicate, that the orgainic Cu-binding ligands might partially be thiols (i.e. similar to glutathione or other sulfur containing peptides [2]) probably produced by design with the pupose to condition the environment.

References

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