

THEME 2: THE DYNAMIC INTERFACE

Session 2.8: Clusters and Nanoparticles

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Study of these materials is new in geochemistry. They lie somewhere between dissolved species and macroscopic solids, but their properties and behaviour are sometimes unexpected. They play a role in mass transport in the environment, in the formation and dissolution of minerals and in geobiology, where they are fundamental to ecosystem function because of their intimate relationship with microorganisms and as moieties in key biochemical processes. We encourage submissions on: the nature of oxide, sulfide, silicate and carbonate clusters and nanoparticles; their structure, composition, and reactivity; the role of clusters in prebiotic synthesis of key biological molecules and in the formation and dissolution of minerals; the mechanisms of reactions between solution species and nanoparticles; the interaction of microbes with clusters and nanoparticles; surface properties of nanoparticles; theoretical considerations of their behaviour and properties; and their environmental significance.

2.8.11

Metal sulfide cluster complexes and their environmental significance

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Metal complexation in oxic waters of the environment has been generally studied with three voltammetric methods - anodic stripping voltammetry, cathodic stripping voltammetry competitive ligand experiments or pseudovoltammetry [1]. The latter gives concentration information on each actual ligand bound to the metal as well as the thermodynamic stability constant of each complex in solution whereas the other two methods give information on conditional stability constants for one complex. Sulfide at low concentrations is also present in oxic waters in addition to anoxic waters of lakes and marine basins. Pseudovoltammetry data (field samples and laboratory solutions) for sulfide complexes with Zn, Cu, Pb indicate that these complexes are not within the thermodynamic stability constant window ($\log K < 40$) of the method and are not simple 1:1 or 1:2 complexes.

Here, we describe how sulfide binds with metals by forming soluble molecular clusters, which have higher thermodynamic stability constants than metal-organic complexes and which are kinetically inert. We present field and laboratory data using a variety of techniques (e.g.; voltammetry, UV-VIS, NMR, ESR, mass spectrometry) to show the existence of metal sulfide clusters for several metals (e.g.; Fe, Cu, Zn, Pb, Ag) with stoichiometries such as $Zn_4S_6(H_2O)_4^{2-}$, $Cu_3S_3(H_2O)_6$. These clusters display the basic structural elements found in minerals and they can react to form higher order clusters, nano-particles and eventually minerals [2] depending on the conditions.

References

- [1] Luther, III G.W., Rozan T.F., Witter A.E., Lewis, B. (2001) Metal organic complexation in the marine environment. *Geochemical Transactions* **9**.
- [2] Rickard D.T. (1997) Kinetics of pyrite formation by the H_2S oxidation of iron(II) monosulfide in aqueous solutions between 25°C and 125°C: the rate equation. *GCA* **61**, 115-134.