Aqueous metal sulfide clusters in marine sediments: Implications for transport, mineral formation and ecology

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Aqueous metal sulfide clusters are nanoparticles or molecular complexes which contain varying numbers of molecules but are small enough to behave as dissolved species. They form a continuum between simple molecular complexes, such as $Fe_2S_2.4H_2O$, $Zn_3S_3.(H_2O)_6$, $Cu_3S_3.(H_2O)_6$, and condensed phases. The clusters display the basic structural elements of the most soluble, least stable, minerals and are implicated in the initial condensation of metastable minerals, such as mackinawite (tetragonal $Fe_{1+x}S$) instead of stable pyrite. Aqueous iron (II) sulfide clusters make a significant contribution to the acid volatile sulfide (AVS) component of anoxic sedimentary systems. The FeS clusters form a continuum of species from molecular Fe_2S_2 up to ca $Fe_{150}S_{150}$. which represents the first observed condensed phase. Molecular Fe_2S_2 is similar in form to the basic structural moiety of crystalline mackinawite. As the sizes of the molecular FeS clusters increase, the Fe-Fe bond lengths and Fe-S-Fe angles increasingly approach those of crystalline mackinawite. This first condensed phase displays a mackinawite structure and has a particle size of ca 2nm. Mass-volume calculations reveal that the formation of pyrite in marine sediments requires that both the Fe and S components of FeS_2 must be transported to the site of pyrite nucleation and crystal growth. The FeS clusters enable transport of Fe in significant concentrations in sulfidic sedimentary environments and are implicated in the development of localized concentrations of pyrite in sediments and organisms. FeS clusters are key components in the formation of sedimentary pyrite. Sediment profiles show that FeS clusters increase in concentration with depth as pyrite concentration increases. Inhibition of cluster formation with, for example, trace aldehydic carbonyl, prevents pyrite formation. The occurrence of FeS clusters has further biogeochemical implications. For example, H_2S is toxic, even to sulfate-reducing prokaryotes (SRP), at relatively low concentrations. The formation of FeS clusters reduces this toxicity by removing a proportion of free aqueous S(-II), allowing further development of SRP. Cluster formation may therefore drive the ecology of anoxic sediments.

References

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Surface charge phenomena of nano-crystalline Anatase

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Crystalline particles of nano-scale dimensions are common in the environment; furthermore, these particles are associated with a variety of surface-geochemical phenomena, including adsorption, precipitation, mineral growth, and ion mobility. It is anticipated that the surface reactivity of nano-scale particles will be dramatically enhanced relative to equivalent macroscopic particles, because thermodynamic properties are modified by small particle size.

Size-dependent surface protonation, and pH_{znpc} and IEP values of nanometer anatase (TiO_2) have been determined by potentiometric titrations and electrophoretic mobility studies. The experimental conditions of the two titration procedures were matched as closely as the different techniques permitted. Four commercially available anatase samples were used in the study, with particle sizes ranging from 200 to <7nm, the corresponding BET surface areas are 10 to 350 m^2/g, respectively. Titrations were performed in NaCl media at ionic strengths from 0.005 to 0.3 molality, at 25ºC. The surface charge of the anatase was enhanced with increasing ionic strength. Moreover, the experimental data suggests that the pH_{znpc} values increase with decreasing particle size.

All experimental data will be rationalized and modeled using the MUSIC surface protonation model of Hiemstra and van Riemsdijk, within the framework of a Stern-based model of the electric double layer (EDL). The MUSIC model provides surface protonation constants explicitly for various types of protolyzable surface groups on a crystal-face specific basis. Modeling of the diffuse layer portion of the EDL will include solutions of the Poisson-Boltzmann equation for spherical symmetry, since at lower ionic strengths the thickness of the diffuse double layer will be similar to the radii of our smaller anatase particles.