

Formation and oxidation of $\text{FeS}_{(\text{aq})}$ molecular clusters: Decoupling iron sulfide mineral dissolution and oxidation reactions

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Iron sulfide molecular clusters, $\text{FeS}_{(\text{aq})}$, are a group of polynuclear iron-sulfide complexes formed under reducing conditions at different modern anoxic or suboxic interfaces in various environmental systems, and are necessary precursors for the formation of iron sulfide minerals [1-5]. Batch and agarose gradient experiments at circumneutral pH show non-stoichiometric, non-oxidative dissolution of mackinawite, pyrrhotite, pyrite, and marcasite minerals with formation of $\text{FeS}_{(\text{aq})}$, illustrating a significant role for $\text{FeS}_{(\text{aq})}$ in the dissolution of Fe-S minerals. Batch and agarose gradient experiments where non-oxidative dissolution products were subjected to oxic conditions indicate no significant formation of intermediate sulphur or sulfoxyanion species in contrast to studies of direct iron sulfide mineral surface oxidation. The dynamic conditions between the formation of the clusters as well as other species in suboxic conditions may thus be a critical component to understanding the cycling of iron and sulfur in a host environments. This suggests significant differences in the reaction pathways for the overall oxidation of iron and sulfur in Fe-S minerals depending on the specific redox environment they occupy.

[1] Theberge & Luther (1997). [2] Rickard & Luther (1997). [3] Wolthers *et al.* (2003). [4] Butler *et al.* (2004). [5] Butler *et al.* (2005).

Mineralogical and geochemical study of PM_{10} in Strasbourg

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The study focused on the mineralogy and geochemistry of airborne particulates (PM_{10}) collected in June 2007 near the centre of Strasbourg at 30 m above ground. An active sampler (Digitel) was used to collect PM_{10} on a teflon filter for subsequent analysis of the bulk chemical composition by ICP-MS. In the entire suite of samples one sample stands out (collected on June 13/14): its bulk chemical composition is characterized by a distinctly larger mass concentration of metals, such as, Pb, Fe and Zn (e.g., ~3x higher than on June 07/08). A second set of PM_{10} samples was collected with an active sampler on carbon filters, which were characterized by SEM using automatic single-particle analysis (Genesis, EDAX). EDS spectra were used for mineralogical classification of the particles. This method revealed a distinct increase in anthropogenic particles on June 13/14 relative to June 7/8. The number of transition metal-bearing particles (e.g., Mn- and Ti-oxide; Fe- and Zn-sulphate) increased by up to seven times. A passive sampler (Sigma-2) was used to collect particulate matter, ranging in size from 2.5 to 10 μm , on a transparent collection plate suitable for automated single-particle optical microscopy. The mass concentrations, calculated from the optical data, revealed a roughly 5-fold increase in anthropogenic particles on June 13/14 compared to the other samples. This considerable difference between the two sampling periods was caused by different meteorological conditions, especially wind direction (N-NE on June 7/8 vs. S-SW on June 13/14), as confirmed by backward trajectories (calculated by NOAA, HYSPLIT MODEL).