



Oxidation of Nanomolar Levels of Fe(II) with Oxygen in Natural Waters

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The oxidation of Fe(II) by molecular oxygen at nanomolar levels has been studied at different pH (6.5 to 8.2), NaHCO₃ (0.1 to 9 mM), temperature (3°C to 35°C) and salinity (0 to 36). The first-order oxidation rates at nanomolar Fe(II) are higher than the values at micromolar levels at a pH below 7.5 and lower than the values at a higher pH. A kinetic model has been developed to consider the mechanism of the Fe(II) oxidation and the speciation of Fe(II) in seawater, the interactions between the major ions and the oxidation rates of the different Fe(II) species. The concentration of Fe(II) is largely controlled by oxidation with O₂ and O₂⁻, but is also affected by hydrogen peroxide that may be both initially present and formed from the oxidation of Fe(II) by superoxide. The model has been applied to describe the effect of pH, concentration of NaHCO₃, temperature and salinity on the kinetics of Fe(II) oxidation. At a pH over 7.2, Fe(OH)₂ is the most important contributing species to the apparent oxidation rate. At high levels of CO₃²⁻ and pH, the Fe(CO₃)₂⁻ species become important. At pH values below 7, the oxidation rate is controlled by Fe²⁺. Using the model, log *k_i* values for the most kinetically active species (Fe²⁺, Fe(OH)⁺, Fe(OH)₂, Fe(CO₃) and Fe(CO₃)₂⁻) are given that are valid over a wide range of temperature, salinity and pH in natural waters. Model results show that when H₂O₂ concentrations approach the Fe(II) concentrations used in this study, the oxidation of Fe(II) with H₂O₂ also needs to be considered.