4.2.P12

Oxidation of iron (II) nanomolar with H_2O_2 in seawater

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The oxidation of Fe(II) with H_2O_2 at nanomolar levels in seawater have been studied using an UV-Vis spectrophotometric system equipped with a long liquid waveguide capillary flow cell. The effect of pH (6.5 to 8.2), H_2O_2 ($7.2x10^{-8}$ M to $5.2x10^{-7}$ M), HCO_3^- (2.05 mM to 4.05 mM) and Fe(II) (5 nM to 500 nM) as a function of temperature (3ºC to 35ºC) on the oxidation of Fe(II) are presented. The oxidation rate is linearly related to the pH with a slope of 0.89 ± 0.01 independent of the concentration of HCO_3^-. A kinetic model considering the speciation of Fe(II) in seawater interacting with the major ions in solution and the oxidation rate of the different Fe(II) species have been developed and applied to the effect of pH, concentration of HCO_3^-, Fe(II) and H_2O_2 and temperature in the Fe(II) oxidation with H_2O_2. $FeOH^+$ is the most important contributing species to the overall oxidation rate from pH 6 to pH 8. At a pH higher than 8, the $Fe(OH)_2$ and $Fe(CO_3)_2^{2-}$ species contribute over 20% to the rates. Model results show that when the concentration of O_2 is two orders of magnitude higher than the concentration of H_2O_2, the oxidation with O_2 also needs to be considered. The rate constants for the five most kinetically active species (Fe^{2+}, $FeOH^+$, $Fe(OH)_2$, $FeCO_3$, $Fe(CO_3)_2^{2-}$) in seawater as a function of temperature has been determined. The kinetic model is also valid in pure water solutions with different HCO_3^- concentrations and conditions found in fresh waters.

4.2.P13

Quantifying the two main processes managing Pb behavior in the Strengbach basin (Vosges, France): Anthropogenic input and weathering

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Pb contents and isotopic compositions were measured in various soil sections as well as in soil waters and surface waters of the Strengbach basin. Detailed analysis of field data (including whole rock and mineral separates) and results of an experimental work, aimed at studying the experimental disssolution of a Strengbach basin granitic rock, lead us to put in evidence and quantify the two major processes managing the Pb behavior in the soil sections:

1. A severe departure of Pb through alteration occurs in the lower parts of the soil which is surprisingly associated with an increase of the Pb isotopic compositions relatively to the substratum rock The Pb departure level could be assessed (using "immobile type" elements references and Pb isotopic budgets) and amounts to 50 to 90% of the initial lead. Contrary to field observations and experimental results indicating a preferential dissolution of Pb isotopic rich phases, the residual soils show a lead isotopic compositional increase relative to substratum. A retention of the previously leached isotopically enriched Pb by secondary formed phosphatic phases is proposed to explain this isotopic rich lead retention. This scenario is supported by mineralogical observations and results of the granite dissolution experimentation performed in the laboratory
2. A significant lead input from atmospheric origin occurs at soil surfaces. Within the soils (from surface to 150 cm depth) this lead input decreases exponentially with depth, following a diffusion law. Diffusion rates vary from one soil section to another being function of multiple physico-chemical factors (organic matter content, drainage…).

Water soils compositions and contents can be understood in that frame. Pb contents in soil solutions increase significantly towards surface levels. A correlation of Pb with dissolved organic carbon (DOC) contents.supports a complexation of Pb with organic matter in these upper soil solutions. Isotopic compositions of soil solutions also vary with depth but they are in isotopic equilibrium with the corresponding soil section only at surface levels. At depth, Pb from soil solutions looks equilibrated with Orthose which is the phase controling most of the rock lead after the previous dissolution of the more isotopic rich minerals.