



Oxidation of Fe(II) by CCl₄ at iron mineral surfaces influenced by pH and organic buffers: a compound specific isotope analysis study

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Carbon isotope fractionation of probe compounds provides mechanistic insights in heterogeneous redox reactions and phase transformation processes taking place at iron minerals under anoxic conditions. Our hypothesis is that such iron phases, mostly present as surface coatings, support an electron cycle by catalyzing heterogeneous oxidation and reduction processes. Iron oxide surfaces may play a key role both as electron acceptors and electron donors due to the high affinity of these iron minerals to dissolved ferrous iron. Repeated sorption and oxidation of Fe(II) may lead to surface structures that are characteristic for a particular geochemical setting. Our overall goal is to evaluate and refine the potential of compound specific isotope analysis (CSIA) to characterize surface mediated redox reactions at iron minerals.

Presently it is very difficult to identify the type and the dynamics of active redox species at mineral surfaces with existing spectroscopic methods. Therefore we propose to develop, validate and apply an indirect method (reactive tracer approach), using compound specific isotope analysis (CSIA). The principle is based on characteristic changes of stable isotope composition of model oxidants upon reaction with different forms of surface bound Fe(II).

The minerals studied include goethite, magnetite, lepidocrocite, hematite and 2-line ferrihydrite. Fe(II) present at iron mineral surfaces is a much more powerful reductant than freely dissolved Fe(II). Tetrachloromethane (CCl₄) is chosen as model oxidant

as its single carbon atom facilitates the interpretation of carbon isotope fractionation. Different environmental conditions like the variation of pH and Fe(II), the simultaneous presence of different minerals and the presence of organic matter (as model compounds such as buffers or NOM) are investigated in terms of their effects on reaction rates, product formation and carbon isotope fractionation of CCl_4 . Results of these ongoing experiments will be presented and discussed in terms of the applicability of isotope fractionation studies to determine surface properties and reactive surface species at iron minerals. Preliminary data suggest that both, pH and presence of organic matter exert strong effects on Fe(II) oxidation at goethite.