Fe(II)-mediated Oxidation of Mn(II)

C. M. VAN GENUCHTEN[1], JASQUELIN PEÑA[1]

[1]Institute of Earth Surface Dyn3amics, University of Lausanne

The oxidation of Fe(II) by O_2 or H_2O_2 produces strong, short-lived oxidants ($^*O_2^-$, $^*OH$, Fe(IV)). These Fenton-type reactants are widely exploited in water treatment and are implicated in the decomposition of organic matter in soils. Recent evidence has also shown that reactive oxidants ($^*O_2$) produced in natural systems (e.g. via photochemical reactions with organic carbon) can oxidize Mn(II). However, the co-oxidation of Fe(II) and Mn(II) in Fenton-type systems has not received attention.

Our objectives in this work are to characterize the reaction products of Fe(II)-mediated Mn(II) oxidation and to determine the factors that control the Mn(II) oxidation efficiency. We employ the Fe(0) electrocoagulation (EC) system, which permits precise control over the rate of Fe(II) production and concomitant reactive oxidants. In all experiments, we investigate the co-oxidation of 200 μM Fe(II) and 100 μM Mn(II) as a function of the iron production rate (IPR), the Fe(II) oxidant ($\approx$ 250 μM O_2 or H_2O_2), and solution pH (3.5 - 8.5). Our approach combines i) time-dependent Mn(II) removal experiments, ii) pyrophosphate (PP) extractions for measurements of Mn(III), and iii) Mn and Fe K-edge EXAFS spectroscopy.

Our results show that Mn(II) oxidation in the Fe(II)/O_2 system increases with decreasing IPR and increasing solution pH, with a maximum Mn(II):Fe(II) oxidation efficiency near 15 mol% at pH 8.5. These trends can be explained by the improved competition of Mn(II) for Fenton-type reactants under conditions that minimize aqueous Fe(II). Although Mn(II) oxidation in the Fe(II)/H_2O_2 system was also most efficient at pH 8.5 (40 mol%), a local maximum in the Mn(II):Fe(II) oxidation efficiency was observed at pH 4.5 (12 mol%). These results are consistent with the pH-dependent products of Fe(II) oxidation by H_2O_2: $^*OH$ is generated at pH < 6, whereas a more selective oxidant (e.g. Fe(IV)) forms at pH > 6. The results from PP extractions and Mn and Fe K-edge EXAFS spectroscopy show that Fe(II)-mediated Mn(II) oxidation yields Mn(III) in all samples, which is coprecipitated or structurally incorporated into lepidocrite (O_2 system) or hydrous ferric oxide (H_2O_2 system).

Our work uncovers a new pathway of Mn(II) oxidation and will help form the basis of Mn(II) oxidation kinetic models in Fenton-type systems. While these reactions can be exploited for Mn(II) removal from water supplies, the consumption of reactive oxidants by Mn(II) must also be considered for accurate predictions of target compound oxidation in Fenton-type systems containing Mn(II).

Water recycling in subduction zones and the role of rehydration in the generation of intermediate-depth seismicity and the nature of the cold fore-arc mantle

PETER VAN KEKEN[1], GEOFF ABERS[2], BRAD HACKER[3], JUNICHI NAKAJIMA[4], SAEKO KITA[5], MARC SPIEGELMAN[6], AND CIAN WILSON[6]

[1]Carnegie Institution of Science, Washington DC, USA, pvankeken@carnegiescience.edu
[2]Cornell University, Ithaca, NY, USA, abers@cornell.edu.
[3]University of California at Santa Barbara, CA, USA, hacker@geol.ucsb.edu.
[4]Tokyo Institute of Technology, Japan, nakajima@geo.titech.ac.jp.
[5]Hiroshima University, Japan, saeko@hiroshima-u.ac.jp.
[6]LDEO, Columbia University, New York, NY, USA, mspieg@ldeo.columbia.edu, cwilson@ldeo.columbia.edu.

Significant amounts of water enter the world's subduction zones in the form of free and mineralogically-bound water. While the free water likely disappears nearly completely at shallow levels, the water bound in rock is released at depth through a series of metamorphic dehydration reactions. Water can move past the volcanic front and be recycled to the deeper Earth particularly in the colder subduction zones.

Geodynamical predictions show that water that is released from the slab travels towards the arc and triggers wet melting in the warm mantle wedge. The released water can also travel back up the slab through the crust and slab wedge. Comparisons with well-determined hypocenters and low-velocity crustal channels in a number of subduction zones suggest the rehydration of the crust and mantle by fluids released from deeper dehydration reactions is likely the cause for intermediate-depth seismicity in these regions by 'rehydration embrittlement'.

These results indicate the importance of hydrological flow in subduction zone processes with potentially significant flow back up the slab. The extent to which these fluids rehydrate the cold fore-arc region of the mantle wedge is still unclear. Seismological observation of this region suggest that in most cases the amount of rehydration and associated serpentinization is modest at best.