Evaluating the role of superoxide (O₂⁻) and hydrogen peroxide (H₂O₂) in the dissolution of Saharan dust in the Tropical Atlantic

M. HELLER AND P. CROOT

IFM-Geomar, Kiel, Germany

(mheller@ifm-geomar.de; pcroot@ifm-geomar.de)

Method and Theory

The major source of iron to the Tropical Atlantic is through aeolian deposition of Saharan dust. Presently within SOPRAN (German SOLAS) we are investigating, at the TENATSO site in Cape Verde, water column processes that control the dissolution of Saharan dust deposited at the seawater surface. The thermodynamic solubility of Fe(III) in surface seawater is thought to be controlled by the presence of iron complexing organic ligands. However in tropical waters, where high fluxes of superoxide (O₂⁻) may exist, due to photochemical reactions of dissolved organic material, there exists the possibility of a kinetic controlled reduction of Fe in colloids and particles to the more soluble Fe(II) [Kustka *et al.*, 2005; Rose and Waite, 2006].

$Fe^{III} + O_2^- + 2H^+ \rightarrow Fe^{II} + H_2O_2$

Photochemistry may not be the only source of O_2^- in seawater as recent work suggests a significant biological source also [Kim *et al.*, 2004]. Overall these processes may lead to longer residence times for dissolved Fe in surface waters [Croot *et al.*, 2004].

Discussion

Current work focuses on laboratory work evaluating analytical methodologies and focuses on three key aspects:

- (i) The influence of temperature on the dismutation rate of O_2^- in seawater.
- (ii) How O_2^- can alter the Fe organic speciation in seawater.
- (iii) Assessment of the enhancement of Fe dissolution from Saharan dust via increased O₂⁻

Conclusion

Using this approach we hope to be able to critically examine the role in which photochemistry and biology play in solubilzing Fe from Saharan dust in Tropical seawater. Overall this information will help in better assessing the key processes controlling iron bioavailability in natural seawater.

References

- Croot, P. L., P. Streu, and A. R. Baker (2004), *GRL*, 31, L23S08, doi.1029/2004GL020153.
- Kim, D., M. Watanabe, Y. Nakayasu, and K. Kohata (2004), Aquatic Microbial Ecology, 35, 57-64.
- Kustka, A. B., Y. Shaked, A. J. Milligan, D. W. King, and F. M. M. Morel (2005), *L&O*, **50**, 1172-1180.
- Rose, A. L., and D. Waite (2006), GCA, 70, 3869-3882.

The reactivity of ferric (oxy)hydroxides toward dissolved sulphide between pH 3 to 9

K. HELLIGE AND S. PEIFFER

Dept. of Hydrology, University of Bayreuth, Germany (katrin.hellige@uni-bayreuth.de; s.peiffer@uni-bayreuth.de)

The reaction between H_2S and ferric (oxy)hydroxides exerts a major role for the sulphur and iron cycle as for the electron and carbon flow in many aquatic systems (e. g. Canfield, 1992). The reaction mechanism is reasonably well understood (Dos Santos Afonso *et al.*, 1992; Peiffer *et al.*, 1992). The reaction rate depends on pH which can be explained by a surface speciation model according to which the electron transfer is preceded by an adsorption step of a sulphide species to the neutral ferric oxide surface >FeOH.

In a recent study, steady-state experiments have been performed at low pH (< 5) using a fluidized-bed reactor that is supplied with a constant flow of electrochemically generated hydrogen sulphide (Peiffer & Gade, 2007). The surface area normalized experimental reaction rates depended on bulk properties of the used minerals and decreased in a sequence Gt > 2lfh > 6lfh. These observations are in contrast to results from batch experiments obtained at pH 7.5 where mineral reactivity seemed to be related to the free energy of their formation (Poulton *et al*, 2004). Under these conditions Fe²⁺ strongly adsorbs to the mineral surface and thereby interacts with dissolved sulfide.

In this study we attempt to resolve these contradictions. Using the same experimental approach as decribed in Peiffer & Gade (2007), we have extended the experimental pH range to study the steady-state reactivity of various iron (hydr)oxides to values between 3 and 9. In this poster we will present the first results from these experiments.

References

- Canfield D. E. and Raiswell R. and Bottrell S. (1992), The reactivity of sedimentary iron minerals toward sulphide. *Amer. J. Sci.* 292, 659-683.
- Dos Santos Afonso M. and Stumm W. (1992), Reductive Dissolution of Iron(III) (Hydr)oxides by Hydrogen Sulfide. *Langmuir* 8, 1671-1675.
- Peiffer S. and Dos Santos Afonso M. and Wehrll B. and Gächter R. (1992), Kinetics and mechanism of the reaction of H₂S with lepidocrocite. *Environ. Sci. Technol.* 26(12), 2408-2413.
- Peiffer S. and Gade W. (2007), Reactivity of ferric oxides toward H2S at low pH. *Environ. Sci. Technol.* In press.
- Poulton, S. W. and Krom M. D. and Raiswell R. (2004), A revised scheme for the reactivity of iron (oxyhydr)oxide minerals towards dissolved sulphide. *Geochim. Cosmochim. Acta.* 68, 3703-3716.