Formation of short-range-ordered Fe(III)-precipitates by Fe(II) oxidation in water

A. VOEGELIN*, R. KAEGI AND S.J. HUG

Eawag, Swiss Federal Institute of Aquatic Science and Technology, Switzerland
(*correspondence: andreas.voegelin@eawag.ch)

We investigated the effect of phosphate, silicate and Ca on Fe (III) precipitates formed by oxidation of Fe (II) in aerated water at pH 7 using X-ray absorption spectroscopy (XAS) [1] and analytical electron microscopy (AEM) [2]. XAS results pointed to the formation of mixed Fe (III)-Ca-phosphates during Fe (II) oxidation as long as dissolved phosphate was present and indicated that Ca affects their structure by linking phosphate-coordinated monomeric or oligomeric Fe (III). In solutions with initial molar P/Fe ratios above ~0.5, mixed Fe (III)-Ca-phosphates were the only precipitates observed. In solutions with initial P/Fe ratios < 0.5, however, XAS showed that formation of Fe (III)-Ca-phosphate polymers was followed by and/or combined with formation of silicate-rich hydrous ferric oxide (HFO-Si) at dissolved Si/Fe ratios > 0.5, 2-line ferrihydrite (2L-Fh) at Si/Fe ratios ~0.1-0.5 or lepidocrocite at Si/Fe ratios < 0.1. AEM results were in line with these observations and additionally indicated that under our experimental conditions (air-saturated solution at pH 7), the different short-range-ordered (SRO) Fe (III) coordination environments (Fe (III)-Ca-phosphate, HFO-Si, 2L-Fh) were either already mixed within individual polymers or that different polymers aggregated into mixed spherical Fe (III)-colloids with uniform composition and structure. However, under conditions favoring slower Fe (II) oxidation (e.g. lower O_2 partial pressure or pH) and faster polymer aggregation and colloid coagulation (e.g. higher ionic strength and shear), distinct Fe (III)-colloids and Fe (III)-flocs dominated by a single type of SRO Fe (III) coordination environment could sequentially precipitate. We therefore hypothesize that solution composition, pH, O_2 partial pressure and shear not only determine the average local Fe (III) coordination of SRO Fe (III)-precipitates but also the spatial scale at which different SRO Fe (III) coordination environments mix in settling precipitates. Such differences in the structure of SRO Fe (III)-phases formed by Fe (II) oxidation at anoxic-oxic boundaries may strongly influence their reactivity and the fate of associated major and trace elements.

[1] Voegelin *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 164–186. [2] Kaegi *et al.* (submitted)

Sources of reactive halogen species and oxygenated VOC over biologically active upwelling reactions of the tropical Pacific Ocean

R. VOLKAMER[1,2]*, S.C. COBURN[1], B.K. DIX[1]
AND R. SINREICH[1]

[1]Department of Chemistry, University of Colorado, Boulder, CO, USA
[2]CIRES, Boulder, CO, USA
(*correspondence: rainer.volkamer@colorado.edu)

About 70% of the Earth's surface is covered by oceans, yet the open ocean marine atmosphere is among the most poorly probed environments of our planet. We have conducted three field campaigns over the tropical Pacific Ocean (133 days at sea), and find reactive gases like glyoxal (CHOCHO), formaldehyde (HCHO) and iodine oxide (IO) are enhanced over biologically active parts of the open tropical Pacific Ocean, more than 3000 km from terrestrial sources. Glyoxal cools our planet by forming secondary organic aerosol (SOA) through processing inside clouds; iodine oxide forms by destroying heat trapping and toxic tropospheric ozone, and forms climate cooling aerosols. These gases are very short lived (atmospheric lifetime is below few hours), and atmospheric transport from terrestrial sources can be ruled out. Our observations locate glyoxal, formaldehyde and iodine oxide inside the marine boundary layer, indicating previously unrecognized sources for reactive halogen species and oxygenated hydrocarbons from the open ocean.