Redox transformations of Cu in periodically flooded soils

B. FULDA[1]*, A. VOEGELIN[2] AND R. KRETZSCHMAR[1]

[1]Insitute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, Switzerland
(*correspondence: beate.fulda@env.ethz.ch)
[2]Eawag, Swiss Federal Institute of Aquatic Science and Technology, Duebendorf, Switzerland

Copper is an essential nutrient, but due to its high toxicity for microorganisms also of concern as soil contaminant. Cu(II) dominates in oxic soils and strongly binds to natural organic matter (NOM). In redox-dynamic environments such as wetland soils, however, periodic flooding and soil reduction may lead to the transformation of Cu(II) to Cu(I) or even Cu(0) [1] and may thereby strongly affect the solubility and mobility of soil Cu. Sulfate reducing conditions during soil flooding may lead to the precipitation of Cu sulfide minerals [1]. However, the soft metal cation Cu^+ probably also exhibits a high affinity to reduced organosulfur compounds, as it is known for other soft metal cations [2].

In a laboratory batch incubation experiment with paddy soil, we therefore investigated changes in the oxidation state and speciation of Cu over a soil reduction-reoxidation cycle as a function of the molar ratio between reducible sulfate and soil Cu (sulfate/Cu 0.1; 0.4; 1.2). Cu K-edge EXAFS data suggested that, after oxic equilibration, spiked Cu(II) mainly adsorbed as Cu(II) to soil organic matter and minerals. During the first few days of soil reduction, a large fraction of soil Cu became reduced to Cu(I) that was complexed by organic thiol groups (based on EXAFS and wet chemical data), and a small fraction was reduced to metallic Cu. During further reduction over 40 days of flooding, Cu was completely transformed to Cu sulfide at high initial sulfate/soil Cu ratio, whereas the Cu(0) fraction increased at low initial sulfate/soil Cu ratio. This difference in Cu speciation during soil flooding also affected Cu speciation after subsequent reoxidation. Whereas metallic Cu was rapidly oxidized to adsorbed Cu(II), a significant part of the S-coordinated Cu(I) remained stable over 14 days of aeration. Our data suggest that metallic Cu may control Cu solubility during soil reduction, especially in sulfate-limited soil. Our data also support the hypothesis that reduction of Cu^{2+} to the much softer chalcophile cation Cu^+ prior to sulfate reduction may induce a shift in Cu-complexation from O/N- to reduced S-functional groups of organic matter.

[1] Weber *et al.* (2009) *Nature Geoscience*, **2**, 267-271. [2] Karlsson *et al.* (2005) *Environ. Sci. Technol.* **39**, 3048-3055.

Coenzyme F430, understanding methanotrophy in methane rich environments

JAMES M. FULTON [1,2], LAURENCE R. BIRD[1] AND KATHERINE H. FREEMAN [1]*

[1]Dept. of Geosciences, Pennsylvania State University, University Park, PA 16802, USA
(*correspondence: khf4@psu.edu)
[2] Marine Chemistry and Geochemistry Department, Woods Hole Oceanographic Inst., Woods Hole, MA 02543, USA

Large amounts of methane are oxidized by communities of methanotrophic archaea and sulphate reducing bacteria, preventing this potent greenhouse gas from reaching the atmosphere [1,2,3]. Methyl-coenzyme M reductase, an enzyme traditionally associated with methanogenesis, has recently been linked also to the anaerobic oxidation of methane [3]. Cofactor F430 is a tetrapyrrole nickel complex contained within the active site of methyl-coenzyme M and appears to be used in both methanogenesis and methanotrophy [3, 4]. Here we present a new approach for purifying F430 from natural samples and determining its stable isotopic composition (^{15}N and ^{13}C). F430 is isolated using multi-dimensional preparatory and high-performance chromatographic separations. Compound identity and purity are confirmed using molar C:N ratios, light absorbance and MS^n detection and fragmentation of F430 isolated from pure cultures of *Methanosarcina acetivorans*. C isotope analyses using nano-EA/IRMS [5] of natural samples are challenged by the presence of co-eluting non-tetrapyrrole structures. Our efforts to date document evidence for F430 in environmental samples, enrichment cultures as well as pure cultures of *Methanosarcina acetivorans*. The identification of F430 in environmental samples potentially provides evidence for anaerobic methane oxidation in a low oxygen environment via the reversal of the enzymes involved in methanogenesis.

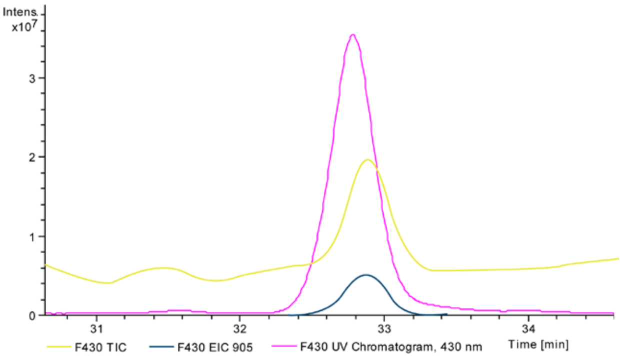

Figure 1: F430 is identified in samples based on adsorption in the 430 nm wavelength and the 905 ion

[1] Orphan (2001) *Science* **293** 5529 484 [2] Orphan (2008) Geobiology **6** 4 376 [3] Scheller (2010) *Nature* **465** 7298 606 [4]Mayr (2008) *Journal Of The American Chemical Soc.* **130** 32 10758 [5] Polissar (2009) *Analytical Chemistry.* **81** 755