Goldschmidt 2021 Abstract
https://doi.org/10.7185/gold2021.7433

Speciation influences copper mobilisation from marine sediments by the chalcophore methanobactin

DANIELLE RUSHWORTH[1], NARESH KUMAR[1], VINCENT NOEL[2], NIELS A.G.M. VAN HELMOND[3], CAROLINE P. SLOMP[3], MORITZ F. LEHMANN[4], WALTER D.C. SCHENKEVELD[5] AND STEPHAN M. KRAEMER[1]

[1]University of Vienna
[2]SLAC National Accelerator Laboratory
[3]Utrecht University
[4]University of Basel
[5]Wageningen University & Research

Presenting Author: danielle.rushworth@univie.ac.at

Marine sediments are huge reservoirs of the potent greenhouse gas methane (CH_4), yet they contribute very little to global net emissions to the atmosphere, largely, due to efficient consumption by a consortium of CH_4 oxidizing microbes. In oxygenated surface sediments and waters, CH_4 oxidation is performed by aerobic methanotrophs *via* methane monooxygenases (MMO), including the Cu-bearing enzyme pMMO which is common to most species. Hence, aerobic methanotrophy in marine sediments is influenced by the bioavailability of Cu, which is often limited by poorly soluble Cu-bearing minerals or organic Cu-complexes, including (oxy)hydroxide, sulfide, and carbonate mineral phases, natural organic matter - metal complexes, and adsorbed species. Under conditions of low Cu availability, some methanotrophs release Cu-binding ligands termed chalcophores, e.g., methanobactin (mb). We observed in our previous work that mb can increase dissolved Cu concentrations even in the presence of insoluble mineral phases like Cu-sulfides.

Through a series of kinetic batch experiments, we investigated Cu mobilisation from a variety of coastal marine sediments in the presence of mb. Results showed that dissolved Cu concentrations were low in absence of mb, however, upon mb addition, dissolved Cu concentrations increased by nearly 7-fold in some sediment suspensions, but not others. Our experimental results suggest that this Cu mobilisation in presence of mb was not correlated to total Cu content, nor was it inhibited by potentially competing metals such as Fe. Cu speciation in the sediments was determined using targeted sequential extraction procedures and X-ray absorption spectroscopy, to elucidate the effect of solid phase Cu speciation on Cu mobilisation. A key finding from this study was that Cu was only mobilised from sediments containing Cu-associated with carbonate minerals, poorly crystalline sulfide minerals or labile metal organic complexes. The efficacy of Cu acquisition by mb in marine sediments is, therefore, strongly influenced by solid phase Cu speciation. Thus, aerobic CH_4 oxidation could be limited in some marine environments.