

Copper sulfide dissolution by methanobactin, a methanotrophic chalcophore

DANIELLE D. RUSHWORTH^{1*}, KEVIN HOFFMANN³, ISO
CHRISTL³, RUBEN KRETZSCHMAR³, WALTER D.C.
SCHENKEVELD², STEPHAN M. KRAEMER¹

¹ Environmental Geosciences, University of Vienna,
Althanstrasse 14 UZAI 1090 Vienna, Austria
(*correspondence: danielle.rushworth@univie.ac.at)

² Environmental Sciences, Copernicus Institute of
Sustainable Development, Utrecht University, Utrecht,
Netherlands

³ Soil Chemistry, Institute of Biogeochemistry and Pollutant
Dynamics, ETH Zurich, Switzerland

Most known methanotrophic bacteria possess the copper (Cu)-bearing enzyme particulate methane monooxygenase (pMMO). It catalyzes the oxidation of methane (CH₄), a potent greenhouse gas, to methanol. Methanotrophic bacteria typically reside in oxic-anoxic interface environments, for example in fresh water lakes. Here, formation of Cu sulfide phases can limit the Cu availability to methanotrophs. Possible phases in these environments include covellite (CuS) and chalcopyrite (CuFeS₂) which are likely to be found as nanoparticles on the order of 10-20 nm. To overcome Cu limitation, certain methanotrophs utilize a Cu acquisition mechanism in which they exude Cu-specific ligands termed chalcophores. One well-elucidated chalcophore, methanobactin (mb), is exuded by the microaerophilic methanotroph *Methylosinus thrichosporium* OB3b.

The basic hypothesis of this project was that mb can increase the solubility and dissolution rates of Cu from sulfide phases at pH values and oxygen partial pressures typical for lake environments where methanotrophs reside. We tested this hypothesis in controlled laboratory experiments, determining the rates and mechanisms of mb-promoted Cu mobilization from Cu-sulfides (bulk and nano-particulate phases) through kinetic dissolution experiments and adsorption experiments under anoxic conditions. We then compared these rates to oxidative dissolution rates of the same phases. We found that mb mobilized Cu over a wide range of pH conditions, including pH 7.5-8.5 where Cu limitation is most likely to occur. We also found that Cu sulfide dissolution at low oxygen partial pressures and in the absence of mb is slow, but that dissolution rates are significantly accelerated by mb. In summary, we show efficient geochemical mechanisms of methanotrophic Cu acquisition from Cu sulfides.