

The effects of amino acids on Cu toxicity for hydrothermal vent microbes

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Microbial life at deep-sea hydrothermal vents is exposed to high concentrations of metals present in the venting fluids (e.g. As, Sb, Se, Cr, Co, Pb, Cd, Ag, Cu, Tl, Zn, Hg). Although some of them are biologically essential at low levels, these metals are toxic at high levels, and non-essential metals may even be extremely toxic at very low concentrations. However, toxicity of a metal for the microbes depends on its chemical speciation, as speciation determines the metal's bioavailability. It has been shown that the biological toxicity of copper is related to the concentration of the free copper ion [1]. Organic molecules, including thiols, constitute ligands capable of forming strong complexes with copper in the hydrothermal environment [2]. There is evidence from culture experiments that organic thiol-containing ligands are actively produced by marine microalgae in response to increasing Cu concentrations, thus reducing its toxicity [3].

We have designed a culture experiment with hydrothermal vent microbes derived from diffuse fluids of the Logatchev hydrothermal field on the Mid Atlantic Ridge at ~15°N to investigate the influence of amino acids (AAs) as possible ligands for Cu, with impact on the bioavailability of both and on the copper's toxicity. The microbes are cultured along Cu gradients (from 0 to 10µM) and with three different concentrations of a mixture of 20 proteinogenic AAs (0, 100nM and 1µM). Furthermore an experiment with just cysteine, a thiol-containing AA, will be carried out, as it is expected to have the strongest Cu-complexing capacity of the AAs.

The concentration of labile Cu, i.e. not complexed by strong organic ligands, of total Cu and of Cu-ligands in the cultures, as well as of the vent sample the microbes are derived of, are measured by voltammetric methods.

[1] Verweij *et al.* (1992) *Chem. Spec. Bioavail.* **4**, 43-51.

[2] Sander *et al.* (2007) *Environmental Chemistry* **4**, 81-89.

[3] Leal *et al.* (1999) *Limnol. Oceanogr.* **44**, 1750-1762.

Linking geochemical signatures and sulphur contents of arc magmas: An experimental approach

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Arc magmas display a characteristic trace element signature determined by the different subducted lithologies, the subduction geotherm and the partitioning behaviour of trace elements between fluids, melts and slab residues. The subducted altered oceanic crust is one source effecting the flavour of arc magmas and it is still debated whether the input occurs via a fluid, a melt or a supercritical liquid [1, 2]. Sulphur (S) preferentially dissolves in fluids opposed to melts, thus the physical state of the slab-derived liquid affects the S mobility. Primitive arc magma compositions preserved as melt inclusions in crystals have S contents up to 3000ppm [3]. Such high S contents plus positive $\delta^{34}\text{S}$ values are commonly attributed to fluids released from subducted sediments [3] because a) the extent of S enrichment in the subducted basaltic crust is not clear and b) S solubility at subduction zone relevant P-T- $f\text{O}_2$ have not been determined.

In an attempt to constrain the trace element and S flux from subducted basalt we carry out a 2 step experimental approach. First, H₂O-saturated crystallisation experiments on a trace element-doped MORB composition are performed at 2.5 to 6 GPa, 750-1100°C and $f\text{O}_2$ -NNO. Second, S saturated experiments with the obtained glass compositions are performed under identical P and T.

Preliminary results show that above the solidus all runs contain gt, cpx, rutile and allanite. Coesite is found to be stable at P > 5 GPa. At 2.5 GPa the glasses are trondhjemitic. At 5 GPa the glasses are granodioritic. With increasing P, D_{Na} in cpx increases and hence Na/K in the melt decreases. The trace element content of the liquid is buffered by the solid residue. A S solubility experiment with a trondhjemitic glass at 2.5 GPa and 900°C shows that S concentrations (1050 ppm) are at least 2 times higher compared to results from lower pressures of 0.2 GPa (~500ppm). From these preliminary results we anticipate that a) increasing P (increasing depth of the slab) explains the change from Na-rich to more K-rich signal in arc magmas and b) S solubility in hydrous liquids increases significantly with increasing P.

[1] Kessel *et al.* (2005) *Nature* **437**, 724-727. [2] Hermann *et al.* (2006) *Lithos* **92**, 399-417. [3] de Hoog *et al.* (2001) *EPSL* **189**, 237-252.