

WHAM- F_{Tox} : An aquatic cation mixture toxicity model

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An important reason for the development of geochemical models of natural waters is to predict and explain toxic effects towards aquatic organisms. We have extended the WHAM chemical speciation model [1,2] for application in toxicity, by assuming that the binding sites of living organisms can be represented by those of humic acid. The calculated cation accumulation (v_i mol g^{-1}), or “active body burden”, measures the exposure of the organism, and is combined with a cation-specific toxicity coefficient (α_i) to quantify the toxic effect via the combined variable F_{Tox} ($= \sum \alpha_i v_i$).

The toxic response is set to zero when $F_{\text{Tox}} \leq F_{\text{Tox,LT}}$ (lower threshold) and 100% when $F_{\text{Tox}} \geq F_{\text{Tox,UT}}$ (upper threshold) with a linear response in between (Figure 1).

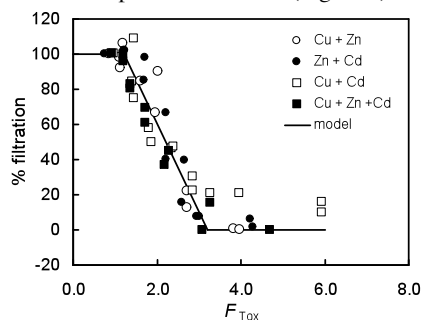


Figure 1: Laboratory toxicity of Cu, Zn and Cd to zebra mussel [3]; data fitted with WHAM- F_{Tox} .

The model has been used to interpret observations of macroinvertebrate species richness in > 400 streams affected by acidification and/or abandoned metal mines [4]. This field application required the use of quantile regression to take into account variations in species numbers due to factors other than the chemical composition of the streamwaters.

[1] Tipping (2002) *Cation Binding by Humic Substances*, Cambridge University Press. [2] Tipping *et al.* (2011) *Environ. Chem.* **8**, 225-23. [3] Kraak *et al.* (1993) *Ecotox. Env. Safety* **25**, 315-327. [4] Stockdale *et al.* (2010) *Aquat. Toxicol.* **100**, 112–119.

Composition of COH fluids up to 2.4 GPa: A multi-method approach

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The mass transfer from the subducting lithosphere to the overlying mantle wedge is mediated by complex solutions resulting from dehydration and decarbonation processes. Compared to H_2O -only and CO_2 -only fluid compositions, experiments dealing with mixed H_2O - CO_2 fluids in equilibrium with high-pressure minerals are limited. In order to investigate the speciation and the solute contents of COH fluids in equilibrium with mantle minerals we performed two sets of experiments at identical P , T and fO_2 conditions using a rocking piston cylinder apparatus. Synthetic forsterite with minor enstatite was used as starting material.

In the first set of experiments we investigate the composition of COH fluids by puncturing the capsule in a gas-tight PTFE vessel at $T=80^\circ C$. Evolved gases were conveyed toward a quadrupole mass spectrometer through a heated line to avoid the condensation of water. Oxalic acid dihydrate and graphite have been used to generate the COH fluid. Experiments were conducted at fO_2 -controlled conditions using NNO, OH (GX, COH) buffer and a double capsule technique. Following thermodynamic modeling we expect in our experiments fluids close to the binary H_2O - CO_2 join.

The second set of experiments was performed to determine the solubility of forsterite in COH fluids. We analyzed the fluid trapped in a diamond layer by the cryogenic laser-ablation inductively coupled plasma-mass spectrometry technique [1]. COH fluids were generated from the addition of graphite, anhydrous oxalic acid and water.

The results will highlight the importance of COH fluids for the mass transport in subduction zones. Comparisons with other experimental systems [2] and with thermodynamic calculations will also be shown.

[1] Aerts *et al.* (2010) *Am. Mineral.* **95**, 1523-1526. [2] Newton & Manning (2002) *Geochim. Cosmochim. Ac.* **66**, 4165-4176.