Mechanisms of Cd, Cu and Zn uptake in jarosite surfaces: A computer simulation study

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Excessive concentrations of metallic elements in soils and groundwater threaten human and ecosystem health, but these elements can be immobilized and their bioavailability reduced by their uptake onto mineral surfaces. An understanding of the mechanisms by which minerals take up metallic elements will underpin the development of effective remediation systems.

Jarosite minerals are effective scavengers of metallic elements, and are abundant in acid rock drainage systems, acid sulphate soils and metallurgical wastes. Jarosite is a member of the isostructural jarosite-alunite group of minerals that has a general formula of $AB_3(TO_4)_2(OH)_6$. The most common member of the jarosite family is potassium jarosite, in which the A site is filled by potassium (K^+), the B site by iron (Fe^{3+}) and the T site by sulphate (SO_4^{2-}), giving $KFe_3(SO_4)_2(OH)_6$. The A and B sites can both be filled by Cd, Cu and Zn.

We have used atomistic computer modelling techniques involving a rigid ion model to investigate the site preferences of Cd(II), Cu(II), Zn(II) in the {012} and (001) faces of end-member K-jarosite. The calculations show that the metallic elements can be incorporated onto the Fe site, but these reactions have high substitution energies and could destabilize the surface. Despite this, calculated solution reactions leading to formation of a new layer of jarosite upon substitution of a metallic cation in the Fe site are exothermic and thus favourable on the $[K(SO_4)_2]^{3-}$ (001) growth face. Substitutions are favoured in the order Cu > Cd > Zn.

Substitutions on the K site are balanced by vacancies on other K sites, and consistently give negative substitution energies and exothermic solution reactions. Substitutions are also favored in the order Cu > Cd > Zn, and $[KFe(OH)_4]^0$ {012} > $[K(SO_4)_2]^{3-}$ (001) > $[Fe_3(OH)_6]^{3+}$ (001) > $[Fe_2(SO_4)_2(OH)_2]^0$ {012}.

TEX$_{86}$ and BIT index measurements in the water column and sediments of a productive coastal fjord

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We used Hood Canal, a fjord situated in Washington State, to investigate the distribution of Glycerol Dialkyl Glycerol Tetraethers (GDGTs) membrane lipids of planktonic archaea and terrestrial bacteria in sinking particles (>60μm) suspended particles (0.7μm - 60μm) and sediments. The GDGTs were used to calculate the TEX$_{86}$ temperature proxy [1] and the BIT index of fluvial terrestrial carbon input [2].
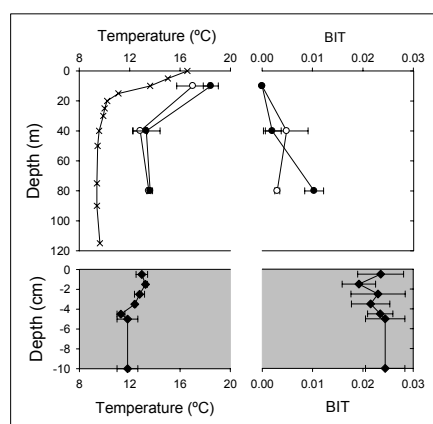

Figure 1: Temperatures from CTD (×), TEX$_{86}$-calculated temperatures and BIT index values for the 60μm (sinking, o) and the 0.7μm (suspended, •) particles and sediment (♦).

Our results reveal that TEX$_{86}$ temperatures did not always reflect *in situ* temperatures measured by CTD (Fig. 1). BIT index values were always very low and sometimes showed differences between large and small particles, Low BIT values likely indicate the small contribution of soil derived carbon in the system [3, 4]. Sediment TEX$_{86}$ and BIT records do not always agree with surface water temperatures or water column BIT index values (Fig. 1). Reasons for the variability between water column and sediment records will be discussed.

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