

## Speciation and mobility of trace elements in wetland soils

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Wetlands including peatlands, riparian floodplains, and paddy soils play key roles in the biogeochemical cycling of carbon, sulfur, phosphorus, and many essential or potentially toxic trace elements (e.g., As, Se, Hg, Zn, Cu, Cd). Understanding the solid-phase speciation, micro-scale distribution, and mobility of trace elements in such soils is an important challenge in soil biogeochemistry. Prof. Willem van Riemsdijk and his coworkers were among the leaders in developing our current understanding of competitive sorption of cations, anions, and NOM to soil mineral surfaces. Competitive sorption of arsenate or arsenite with other anions such as phosphate or carbonate, for example, are now rather well understood and can be modelled quantitatively using the CD-MUSIC approach [1]. However, sorption and speciation changes of trace elements during reduction/oxidation cycles in soils, often coupled to iron mineral transformations and sulfur redox reactions in the presence of NOM, are still poorly understood. We therefore explored the influence of soil flooding on trace element speciation and mobility and found formation of metallic Cu(0) and metal sulfide nano-particles by suspended bacteria to be an important mechanism controlling pore water concentrations of Cu, Hg, Zn, and Pb [2]. More recently, we explored the speciation of As in different wetlands and found As(III) bound to reduced sulfur groups of NOM to be the dominant species in anoxic peat layers [3]. Subsequent model studies confirmed this newly discovered binding mechanism of As to NOM [4], which may of great importance in other NOM-rich, reducing environments. In contrast, in a mining-affected river floodplain, As was mainly present as As(V) coprecipitated with Fe(III) in poorly-crystalline mineral phases, exhibiting similarity to amorphous ferric arsenates, partly forming rims around weathering pyrite and arsenopyrite grains. The solid-phase speciation greatly influences the kinetics of microbial Fe and As reduction and release, and is therefore important for understanding As release under reducing conditions in soils [5].

[1] Stachowicz *et al.*, *J. Colloid Interf. Sci.* **320**: 400, 2008. [2] Hofacker *et al.*, *Geochim. Cosmochim. Acta* **103**: 316, 2013. [3] Langner *et al.*, *Nature Geoscience* **5**: 66, 2011. [4] Hoffmann *et al.*, *Environ. Sci. Technol.* **46**: 11788, 2012. [5] Weber *et al.*, *Environ. Sci. Technol.* **44**: 116, 2010.

## Juvenile crustal growth during the Palaeoproterozoic: U-Pb-O-Hf isotopes of detrital zircon from Ghana

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The Palaeoproterozoic domains of the West African Craton (WAC) (~2.15 Ga) have been described as a fast growing segment of juvenile crust based on geochronological data and Nd-model ages. Detrital zircon from four rivers in Ghana, southeastern WAC, were analysed for U-Pb, O and Lu-Hf isotopes and a zircon population from a fifth river was analysed for U-Pb and Lu-Hf isotopes. U-Pb crystallisation ages mainly cluster between 2.24 and 2.09 Ga with a peak at ~2.14 Ga, reflecting peak magmatic activity. The zircon population from the Birim river, representing the Kibi-Winneba belt, in southeast Ghana have zircon with U-Pb ages >2.2 Ga, which is nearly absent in other rivers.

The entire zircon population has  $\epsilon_{\text{Hf}}$  values ranging from 0.9 to 7.1, except four grains from the Birim river population that have negative  $\epsilon_{\text{Hf}}$ . Although there are contrasts between the zircon populations from the different rivers, the data imply relatively juvenile crust without any significant reworking of ancient crustal components. ~2.2 Ga zircon from the Birim river have depleted  $\epsilon_{\text{Hf}}$ , while a younger (2.15 Ga) subset of zircon requires a reworked Archaean component. Zircon from Sihili and Black Volta rivers form a loosely defined trend that suggest the reworking of mafic crust, while the others do not.

Contribution of reworked supracrustal rocks were minor during the initial growth stages as indicated by the absence of zircon with  $\delta^{18}\text{O} > 6.5\text{‰}$  prior to 2.174 Ga. The proportion of grains with elevated  $\delta^{18}\text{O}$  gradually increases after 2.174 Ga, suggesting increasing amounts of reworked supracrustal sedimentary components. However, these zircon grains with high  $\delta^{18}\text{O}$  have depleted  $\epsilon_{\text{Hf}}$ , which suggests fast reworking of young supracrustal rocks, perhaps in a maturing arc system.