

## Mo isotopes in Archean carbonates: Ocean water evolution, atmospheric oxygen and sulfidity levels

A.R. VOEGELIN<sup>1\*</sup>, T.F. NÄGLER<sup>1</sup> AND N.J. BEUKES<sup>2</sup>

<sup>1</sup>Inst. of Geological Sciences, University of Bern, Switzerland  
(\*correspondence: voegelin@geo.unibe.ch)

<sup>2</sup>Dept. of Geology, University of Johannesburg, South Africa

We present carbonate Mo isotope data of the 2.64-2.5Ga old Ghaap Group (Transvaal Supergroup, South Africa) to address the debate on early Earth oxygenation. Non-skeletal carbonates have been proposed as a monitor of ambient seawater  $\delta^{98/95}\text{Mo}$  because fractionation upon Mo uptake is minimal and their isotopic composition independent of local redox conditions [1]. As a first order approach we therefore consider the investigated Archean carbonates to represent the isotopic evolution of the ambient seawater through time. The record is characterized by three phases of heavy  $\delta^{98/95}\text{Mo}$  values interrupted by two shifts towards detrital levels. This nearly continuous presence of fractionated Mo suggests a quasi permanent availability of at least small amounts of free atmospheric  $\text{O}_2$  during the deposition of the Ghaap Group sediments. Furthermore, the data of this study are compared to the results of [2], who investigated intercalated shales from the same drill core. In anoxic sediments the behavior of Mo is fundamentally different as their Mo isotopic composition is controlled by sulfidity levels in the depositional environment. Below the critical  $\text{H}_2\text{S}_{\text{aq}}$  concentration of  $11\mu\text{M}$ , fractionation is as significant as in oxic sediments [3]. Consequently, black shales do not per se archive the coeval seawater signature and only a minimum value is provided. Considering the different geochemical behavior of the two archives with respect to Mo, we postulate that the combined records can be used as a qualitative measure of the extent of water mass sulfidity during black shale sedimentation. Coincident heavy carbonates and light shales are indicative of non-quantitative Mo scavenging during suboxic/weakly euxinic black shale deposition. In conclusion, we propose that the Ghaap Group carbonates provide a more precise reconstruction of the long term evolution of the  $\delta^{98/95}\text{Mo}$  of the ambient water mass than do black shales. The interpretation of the oxygenation history, however, profits from the comparison of the two records and gives new insights into the extent and timing of the occurrence of atmospheric oxygen. The general interpretation of both cores is identical: atmospheric  $\text{O}_2$  was present before 2.5 Ga ago.

[1] Voegelin *et al.* (sub.). [2] Wille *et al.* (2007) *GCA* **71** 2417–2435. [3] Neubert *et al.* (2008) *Geology* **36** (10), 775–778.

## Multi-metal dynamics during reduction of freshwater floodplain soil under sulfate-limitation

A. VOEGELIN\*, F.-A. WEBER AND R. KRETZSCHMAR

Institute of Biogeochemistry and Pollutant Dynamics,  
ETH Zurich, Switzerland

(\*andreas.voegelin@alumni.ethz.ch)

Riparian soils are often polluted with a variety of metal contaminants, which might be released to ground and surface water during periodic flooding. Under sulfate-reducing conditions, formation of sparingly soluble metal sulfide precipitates can control the mobility and bioavailability of chalcophile metal contaminants. However, the moderate sulfate availability in freshwater floodplain soils may limit the extent of metal sulfide formation, complicating the prediction of multi-contaminant systems.

We studied the dynamics of Cu, Cd, Pb, Zn, and Ni in a contaminated floodplain soil under a sulfate-limited flooding regime over 7 weeks in microcosm experiments. Most contaminants were initially mobilized by competitive sorption of Fe(II) and Mn(II) and by dissolved organic matter release. During sulfate respiration, available sulfate ( $\sim 2.3\text{ mmol/kg}$ ) was transformed into chromous reducible sulfide (CRS), whereas soil organic matter (SOM) mineralization was an insignificant sulfide source over 7 weeks. X-ray absorption spectroscopy showed that soil Cu was initially SOM-bound Cu(II). Up to 17% Cu were intermittently transformed into metallic Cu(0), and 66% of the total soil Cu were sequestered into  $\text{Cu}_x\text{S}$  after 7 weeks.  $\text{Cu}_x\text{S}$  was the dominant sulfide phase accounting for most of the CRS. Sequential extractions, suggested that, in addition to Cu, easily mobilizable Cd was completely and Pb partly sequestered in sulfide precipitates, resulting in a marked reduction of dissolved Cd and Pb. In contrast, Zn and Ni (and also As and Fe) were hardly incorporated into sulfide phases and dissolved concentrations remained constant (Zn) or even increased (Ni) during soil reduction. The finding that Cu, Cd, and Pb formed sulfides, whereas Zn, Ni, and Fe did not, can be explained by the increasing solubility products of the respective metal sulfides. The observation that Cd and Pb formed sulfides while some SOM-bound Cu(II) remained further indicated the influence of the kinetics of metal supply and sulfide precipitation.

We conclude that the dynamics of multiple chalcophile metal contaminants in sulfate-limited freshwater floodplain soils are intimately coupled by competitive sorption and competitive metal sulfide formation, the latter being controlled by the thermodynamic stabilities and formation kinetics of metal sulfides.