

## Copper and zinc isotope fractionation during their interaction with phototrophic biofilm

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In geochemistry, the study of the interactions between trace metals (TM) and aquatic microorganisms is limited essentially by the characterisation of surface's interactions for short exposure time and for uptake experiments for selected monospecific groups of algae and bacteria. The originality of our work is to combine the study of Cu and Zn isotope fractionation with biological characterisation of phototrophic biofilms during long incubation times in order to allow for the integration of an ecological dimension.

Towards this goal, batch and open flux experiments including trace metals (TM) sorption, incorporation and extracellular release were performed on mature biofilm having a cyanobacterial dominance. Moreover, the impact of temporary drying on metal release from biofilm was studied. Another experiments were performed in Taylor Couette reactor to study the relation between a biofilm growth cycle and the degree of stable isotope fractionation during metal uptake.

Results show that in batch reactor, the pattern of metal isotope fractionation is dramatically different between Zn and Cu. There is an accumulation of heavy Zn isotope in the biofilm during the first 96 hours with an average isotopic shift close to  $0,3 \pm 0,1 \text{ ‰}$ . In contrast, the copper interacting with biofilm during 48 hrs is enriched in light isotopes (approx  $0,16 \pm 0,07 \text{ ‰}$ ) but later this trend is reversed bringing to enrichment the biomass in heavy isotope. The observed difference may be linked to (i) the different toxicity of metal with Cu being more toxic than Zn and (ii) the difference of physicochemical properties of metal interaction reactions: internalization of copper is faster than that of Zn and only Cu could undergo redox reaction within the biofilm matrix and inside the cells.

Our results provide firm basis for establishing the link between metal complexes structure and toxicity and the degree of stable isotope fractionation that can be used for tracing biological processes in natural waters.

## Montalto Formation: A Middle Cambrian to basal Ordovician sequence in Dúrico-Beirã area (Northern Portugal)

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Montalto Formation [1] occur in Dúrico-Beirã area (northern Portugal) in Central-Iberian Zone. It's formed by three lithologic associations. The Lower lithologic association is mainly composed of grey and violet slates with intercalations of altered volcanic acid rocks and exhalites. The Intermediate lithologic association is composed by alternating sequences of slate, quartzite, and subordinate wacke. The Upper lithologic association is mainly composed of conglomerates usually clasto-supported with minor pelite, siltite, quartz arenite and wacke intercalations. Some conglomerates are well calibrated dominantly bearing quartz clasts usually elongated and orientated. Other conglomerates occurring to the top of the sequence are polygenic, poorly calibrated with clasts of varied nature (quartz, schist, black quartzite) intersperse with pelitic or quartzitic layers evidencing a more superficial facies, probably continental. Dykes of diabase are particularly frequent in this lithologic association. This formation overlies the Terramonte Formation [1], a thick flyschoid sequence, showing some turbiditic characters being equivalent to Desejosa Formation defined in Douro Group (Lower Cambrian to Middle Cambrian) [2]. Montalto Formation underlies a lithologic association mainly composed of conglomerates, quartz-arenites, minor pelites and wackes interbedded with volcanic rocks exhibiting bimodal composition (volcanoclastic rocks of rhyolitic affinities and basic volcanic rocks) that evidence a continental rifting [3] of probably Tremadocian age. To the top the Armorican quartzites occur (Floian). So, an age between Middle Cambrian and basal Ordovician (Tremadoc) is proposed to Montalto Formation. This contrast to a Floian age proposed by some authors [4] when correlating Montalto Formation to Vale de Bojas Formation and Eucísia Formation (Trás-os-Montes). These last formations can be correlated to the volcano-sedimentary sequence of probable Tremadocian age [3].

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