

Carbon and nitrogen isotopes cycling recorded in sediments from anoxic and ferruginous Lake Pavin

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Over geological timescale, the Earth's oceans were affected by several periods of total or partial anoxia. Timing, causes and consequences of the ocean oxygenation can potentially be better understood from past C and N cycles. Studies on modern analogues are essential for interpreting the biogeochemical signal recorded in ancient sediments. Lake Pavin (French Massif Central) is permanently stratified with anoxic Fe-rich deep waters (from 60 to 92m depth) overlain by oxic shallow waters (from 0 to 60m depth) and can be regarded as an analogue for the ocean during periods of redox stratification with ferruginous deep water column.

In order to determine if the primary C and N isotope signatures are preserved or modified in this type of environment, we analyzed bulk C and N isotope compositions in 3 sediment cores from different depths in Lake Pavin: in the oxic zone (31.5m depth), at the oxic-anoxic boundary (60m depth), and the last one at the peak of H₂S production from SO₄²⁻ reduction (65m depth). For the cores of the anoxic layer the C and N isotopic compositions show little variability: $\delta^{13}\text{C}_{\text{org}} = -26.8 \pm 0.4\text{‰}$ (1 σ) and $\delta^{15}\text{N}_{\text{tot}} = -1.1 \pm 0.2\text{‰}$ (1 σ). Such $\delta^{15}\text{N}$ values suggest a dominance of N₂-fixers in the water column, which is expected in stratified system where nitrates are strongly denitrified at the redox boundary. For the core of the oxic layer, both $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{tot}}$ increase with depth, from -28.6 to -25.3‰ and -3.4 to -1.7‰, respectively. This variation indicates either a modification of the primary signal by oxic early diagenesis or a change of the biomass contributing to the isotopic signal. Further investigations are still needed to explain this variability.

Preliminary analytical approaches to investigate the biogeochemical role of selenomethionine in aquatic ecosystems

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Recent changes to legislation relating to acceptable environmental selenium (Se) concentrations in North America have provided an increased need to better understand the element's natural biogeochemical cycle. Although toxicity tests modeling parts of this cycle generally expose organisms to the organic Se species selenomethionine (SeMet), to our knowledge it has not been shown that this form of Se is present in the abiotic compartments of the natural environment for uptake in real ecosystems.

It is well established that algae, the lowest trophic level in most aquatic systems, have the ability to uptake inorganic Se and metabolize it into SeMet – as both free and proteinaceous forms.[1] For this reason, as a preliminary investigation into the ability of SeMet to be released from organisms (upon their death) back into their surrounding environment, we have grown algal cultures (3 species of *Chlorophyta* and 1 *Cyanobacterium*) in the presence of selenate and examined the resulting metabolites that are present both within the cells and released into the growth media.

For the analysis of SeMet and other metabolites we have optimized existing anion-exchange chromatography inductively-coupled plasma mass spectrometric (AEC-ICP-MS) methods to allow for baseline resolution between various organic Se species of similar retention, while still allowing for quantitative analysis of inorganic metabolites such as selenite and selenocyanate. Using this method it has been observed that free SeMet is one of the main Se species within algal cells though only trace amounts are found in the growth media; potentially due to efficient re-uptake after this metabolite is released. To further confirm the identity of SeMet in algal growth media, electrospray tandem mass spectrometry (ES-MS/MS) was used and characteristic fragmentation patterns of the molecular ion were observed for various isotopes of Se.

The overall goal of this work involves determining whether SeMet is present in the abiotic compartments of the natural environment, which would make it available for uptake into the lowest trophic level of aquatic food webs and likely play a vital role in the initial stages of Se toxicity in these ecosystems. Preliminary evidence of discrete organic Se species in an impacted river system, as well as the potential implications of this will be discussed.

[1] Fan *et al.* (2002) *Aquat. Toxicol.* **57**, 65-84