

## Carbon cycling in hypertrophic Lake Baldegg (Switzerland), with implications for eutrophication models

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Several studies established the isotopic composition of carbon as a valuable proxy for past changes in nutrient loading, productivity and carbon cycling in lakes. In lake systems where primary productivity is the principle control on carbon cycling, enrichment in <sup>13</sup>C of organic matter is generally interpreted to indicate an increase in productivity in response to seasonal changes, anthropogenic eutrophication and/or long-term environmental change. However, recent studies have recognized that microbially mediated carbon cycling processes, associated with development of anoxic conditions in the water column, can also impart a distinct isotopic signature to sedimentary carbon which is significantly depleted in <sup>13</sup>C relative photoautotrophic biomass (Hollander and Smith, 2001).

We investigated carbon isotopes ( $\delta^{13}\text{C}$ ) for organic matter,  $\text{CaCO}_3$  and dissolved inorganic carbon from Lake Baldegg, a deep, hypertrophic lake in Central Switzerland, in order to assess controls on both seasonal and longer-term carbon cycling. Figure 1 presents the response of organic carbon  $\delta^{13}\text{C}$  values, from seasonally resolved sediment core samples, to documented changes in nutrient loading, water column anoxia and lake restoration over the last ~120 years.

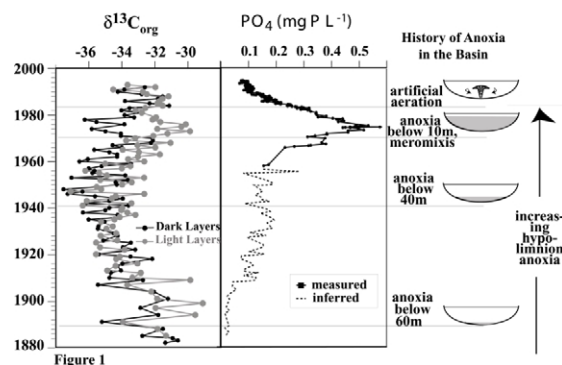


Figure 1

During the period of most intense eutrophication, the carbon isotope signal predictably reflects increasing input of eukaryotic productivity. However, the early decrease in  $\delta^{13}\text{C}$  values illustrate the influence of microbially mediated carbon in response to initial nutrient loading and increasing anoxia. From these results we refine various eutrophication models in order to better describe the changing influence of <sup>13</sup>C-depleted microbial biomass relative to <sup>13</sup>C enriched photoautotrophic biomass on the  $\delta^{13}\text{C}$  record of sedimentary carbon in both modern and ancient lake systems.

## Iron isotope fractionation in groundwater

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We have measured Fe isotope compositions to characterize Fe during an in-situ water treatment for removal of dissolved Fe and Mn from drinking water. Large isotopic variations of Fe were measured during the field experiment in a reduced Fe-containing groundwater.

Injections of aerated water into the aquifer, leading to precipitation of Fe<sup>II</sup>-hydroxides (FeOOH), followed by extraction of groundwater were performed in five cycles. Fe<sup>II</sup> is strongly depleted after injection due to adsorption on FeOOH and increases during extraction due to return of surrounding Fe<sup>II</sup>-rich water.

$\epsilon^{57}\text{Fe}/^{54}\text{Fe}$  ( $2\sigma$  typically 1.2‰, normalised to IRMM-014 standard) were measured for water sampled throughout cycles #2 and #5. Before the field experiment  $\epsilon^{57}\text{Fe}/^{54}\text{Fe}$  is lighter compared to typical crustal Fe, due to fractionation during microbial dissolution of FeOOH in the aquifer.  $\epsilon^{57}\text{Fe}/^{54}\text{Fe}$  in cycle #2 varied with time from -35 to -7.5 and were linearly correlated with Fe concentrations (0.12 to 1.38 mg/l,  $R^2=0.974$ ). Adsorption of Fe<sup>II</sup> from the surrounding isotopically heavier groundwater on the newly formed FeOOH produces very light groundwater. With time, the adsorption sites for Fe<sup>II</sup> in the system decrease, Fe<sup>II</sup> in the water increases and consequently,  $\epsilon^{57}\text{Fe}/^{54}\text{Fe}$  becomes heavier. This linear pattern was reproduced in cycle #5 for the major part of the Fe<sup>II</sup> increase ( $\epsilon^{57}\text{Fe}/^{54}\text{Fe} = -34.1$  to  $-19.4$ ; Fe<sup>II</sup> = 0.31 to 0.87 mg/l). However, in the first extracted water (Fe<sup>II</sup> = 0.13 and 0.21 mg/l),  $\epsilon^{57}\text{Fe}/^{54}\text{Fe}$  is somewhat heavier than expected from the correlation (-26.6 and -32.8, respectively). This observation needs further examination to draw conclusions on the processes involved.

Abiotic Fe<sup>II</sup> adsorption on FeOOH appears to be responsible for the Fe fractionation because (i) the abiotic oxygenation of Fe<sup>II</sup> is very fast under the conditions in the groundwater and out competes microbial processes and (ii) bromate (alternative oxidant) injected into the groundwater showed the same retention pattern for Fe<sup>II</sup> as oxygen.

It is emphasised that our study was performed in natural groundwater with low iron levels, in contrast to most previous studies. The generation of very light Fe isotopic compositions, the linear relationship between  $\epsilon^{57}\text{Fe}/^{54}\text{Fe}$  and Fe concentrations, and the reproducibility of these characteristics provide strong constraints on iron behaviour in groundwater.