Si isotope signatures preserved in BSi hold temperature information

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High-latitude aquatic ecosystems of the subarctic and arctic region have been shown to be influenced by climate fluctuations on short growing seasons for diatoms[1]. In our study[2], we reconstructed diatom production in Bothnian Bay, the subarctic northern tip of the Baltic Sea, by analysing Si isotopes in biogenic silica (BSi) perserved in sediments using MC-ICP-MS. The sediment core dated by ^{210}Pb gamma-ray spectrometer covered the period of 1820 to 2000, consisting of an unperturbed period from 1820 to 1950 and a second period affected by human activities from 1950 to 2000. The Si isotope values ranging between δ^{30}Si −0.18‰ and +0.58‰ in BSi were used to infer diatom production by using the Rayleigh model for fractionation patterns (Fig. 1). This exhibited that the production was correlated with air and water temperature, which in turn were correlated with the mixed layer depth. Especially after cold winters and deep water mixing, diatom production was limited. We also observed a shift of Si isotope values in the sediments after 1950, which is most likely caused by large scale damming of rivers which was heavily carried out between 1940 and 1960. Our findings offers a new way to estimate diatom production over much longer periods of time in diatom dominated aquatic systems, i.e. a large part of the world's ocean and coastal seas.

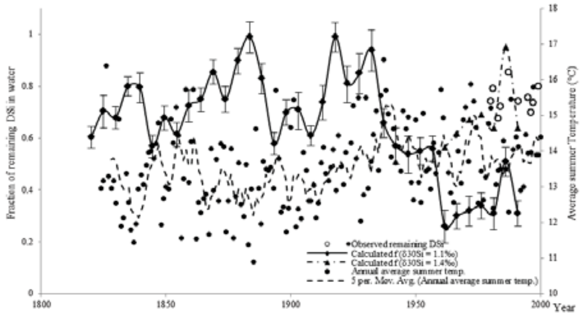

Figure 1: Fraction of the remaining DSi (f) in the water column reconstructed by the Rayleigh model, plotted with average summer air temperature through years. The inferior and superior error bars on f -values are the first quartile and third quartile for each f -value[2].

[1] Douglas & Smol (2010), The diatoms: applications for the environmental and earth sciences, *Smol J.P. & Stoermer E. F. eds, 12,* 231-248. [2] Sun et al. (2011) *Biogeosciences* **8**, 3491-3499.

EXAFS studies of Fe speciation in natural stream waters

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Introduction

Fe speciation in organic rich soils and aquatic environments depends on the interactions between Fe and natural organic matter (NOM)[1]. These interactions also have a large influence on the availability of nutrients such as phosphorus and thus on biological productivity in natural environments. Accordingly, the Fe-NOM interactions are of fundamental importance but the generally low Fe concentrations in natural stream waters prevent direct spectroscopic studies. In this work we have developed a gentle and non-invasive method for concentrating stream water samples using adsorption via electrostatic forces onto permanently charged particles. The Fe speciation in these samples was subsequently analyzed by means of EXAFS spectroscopy. Stream waters were collected at the well-studied Krycklan Catchment[2], 64°, 16'N, 19°, 46E, in northern Sweden, with Fe concentrations in the range of 8-40μM.

Results

EXAFS investigations of negatively charged metal model complexes concentrated by our method showed that no significant distortions were induced as compared to the solution structures, which is in accordance with previous results[3,4]. The local structures of Fe(III) complexes in stream water samples from a forested site were investigated by applying the same technique. The EXAFS results indicated that the Fe(III) speciation was dominated by mononuclear organic chelate complexes and hydrolyzed Fe with ferrihydrite-like structures. We have also performed EXAFS studies of Fe speciation in soil solutions and groundwater, and these results will also be discussed. Finally, the method is not limited to EXAFS and we will show how it can be applied to P-NMR studies of natural waters, facilitating differentiation between inorganic and organic phosphorus species.

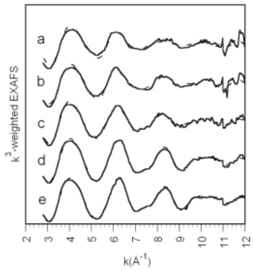

Figure 1. k^3-weighted EXAFS data from stream waters collected at the Krycklan Catchment[2], in February 2010, for a gradient series with a) 100%, b) 84%, c) 77%, d) 42% and e) 28% adsorption of Fe from the stream water. Solid lines represent experimental data and broken lines are fitted data.

[1] Rose et al. (1998) *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **136**, 11-19. [2] Laudon et al. (2011) *Ecosystems* **14**, 880-893. [3] Bargar et al. (1999) *Geochimica et Cosmochimica Acta* **63**, 2957-2969 [4] Kaplun et al. (2008) *Langmuir* **24**, 483-489