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1 Assessing the meaning of trace elements incorporated in biogenic opal: an integrated field and laboratory approach

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Previous research has shown that the elemental stoichiometries of marine and freshwater algae reflect both the nutrient ratios of the aquatic environment and control the input of recycled elements through remineralization. Although most attention has been focused on the C, N and P content of plankton a growing number of recent studies have concentrated on the algae trace metal composition. The often controversial evidence that trace metal nutrients such as iron can limit primary production in both open-ocean and coastal environments has encouraged researchers to further study the trace metal content of plankton. Our study aims to identify and quantify the influence of the processes controlling the incorporation of trace elements in the frustules of selected diatoms in order to evaluate the use of this technique as a new proxy for past water conditions. To achieve this task, we combine high-resolution field analyses with selected laboratory experiments.

In a first effort to test the potential of the elemental composition of recent diatom frustules to reconstruct the known polluted history of a natural system, a pilot study was conducted in Lake Geneva modern sediments. A short sedimentary core was retrieved in the central part of the lake and was sampled following a "range finding" strategy. The first challenge was to develop an efficient and *friendly-to-use* methodology to separate and clean the frustules from the clay-dominated sediments. Once this was achieved, a selected number of samples were inspected with SEM to insure the total absence of clay fragments that could jeopardize the results. The samples containing the isolated diatom fraction were dissolved and analysed by ICP-MS. Preliminary results showed that the incorporation of different trace elements into the frustule has substantially changed throughout the studied time interval. A similar trend characterized most of the analysed metals (Al, Ca, Ti, V, Cr, Mn, Fe, Ga, Rb, Sr, Ba, Pb) with comparatively higher concentrations for the last half of the twentieth century. Some other elements such as Sc seemed to follow the opposite trend whereas Zn showed a more scattered distribution.

Currently, laboratory experiments with diatom cultures are performed under controlled conditions in order to determine the influence of concurrent parameters on the incorporation of trace elements in the opal structure. Long-term Zn, Cd, and Pb uptake experiments are run with *Stephanodiscus hantzschii*, a small centric freshwater diatom representative of today's Lake Geneva main diatom assemblages.

The combination of these ongoing laboratory experiments and field studies, as well as the confrontation of these data with the recent history of anthropogenic pollution of lake Geneva provide a unique opportunity to test and calibrate this proxy.