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## PUBLICATION

T. Schäfer, V. Chanudet, F. Claret, and M. Filella, "Spectromicroscopy Mapping of Colloidal/Particulate Organic Matter in Lake Brienz, Switzerland," *Env. Sci. & Technol.*, **41**, 7864-7869 (2007).

V. Chanudet and M. Filella, "Submicron Organic Matter in a Peri-Alpine, Ultra-Oligotrophic Lake," *Org. Geochem.*, **38**, 1146-1160 (2007).

## FUNDING

Regional government of the Canton Bern; Kraftwerke Oberhasli (KWO); Bundesamt für Umwelt (BAFU); Lake Brienz shoreline communities

## FOR MORE INFORMATION

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## Characterization of Natural Organic Matter in an Ultra-Oligotrophic Lake

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*Low-nutrient, or oligotrophic, alpine lakes showing very small quantities of natural organic matter (NOM) have attracted increased interest over the past few years as they are sensitive indicators for a wide variety of anthropogenic stressors including climate changes. We have used a combination of microscopic and spectroscopic tools to investigate the role of mineral colloids and organic macromolecules in Lake Brienz (Switzerland) and its tributaries, the Aare and Lütschine Rivers in creating and/or maintaining severe oligotrophic conditions. Evidence gleaned from transmission electron microscopy (TEM), scanning transmission x-ray microscopy (STXM), and ultra-Fourier transform infrared spectroscopy ( $\mu$ FTIR) shows that NOM sorption onto inorganic settling particles mainly causes the elimination of NOM in the lake (estimated to be 25% from mass balances).*

Combining spectromicroscopic methods with NOM measurements using the classical MBTH (3-methyl-2 benzothiazolinone hydrochloride) method for carbohydrate determination and a new voltammetric method for the determination of refractory organic matter (ROM) made it possible, for the first time, to quantify the types, functionalities, sources, and fate of submicron NOM present in an ultra-oligotrophic lake (Lake Brienz, Switzerland) and its two tributaries, the Aare and Lütschine rivers (**Figure 1**).

NOM concentrations remained extremely low throughout the year ( $<1$  mg C·L<sup>-1</sup>) with carbohydrate concentrations of 0.06–0.43 mg C·L<sup>-1</sup> in the lake and 0.06–0.25 mg C·L<sup>-1</sup> in the

two tributary rivers. Pedogenic ROM is a major source of organic material in Lake Brienz with concentrations in the lake of 0.1–0.2 mg C·L<sup>-1</sup>. Melting snow was responsible for about 32% of the lake's annual ROM input. The concentration of all types of NOM is at its lowest after lake mixing. One box mass balance calculations showed that about 25% of ROM was lost within the lake that is not accounted for by lake flushing.

Principal component (PCA) and

cluster analysis of C1s STXM data of a lake water sample (1 m depth) revealed spectroscopically different regions with a cluster (**Figure 2**, yellow region) showing a general high optical density (spectra not shown) and no spectral features typically for purely inorganic minerals. Cluster 1 (**Figure 2**, red region) has a high absorption at the potassium L<sub>2,3</sub>-edge (orthose, biotite or illite minerals), but relatively weak absorption on the carbon edge (optical density OD  $\sim$ 0.05). Finally, higher amounts of organic structures (OD  $\sim$ 0.12) can be found (**Figure 2**, green region), either surrounding these inorganic phases as submicron colloidal structures/coatings or as separate submicrometer sized par-



Authors (from left) Vincent Chanudet and Montserrat Filella, Thorsten Schäfer, and Francis Claret

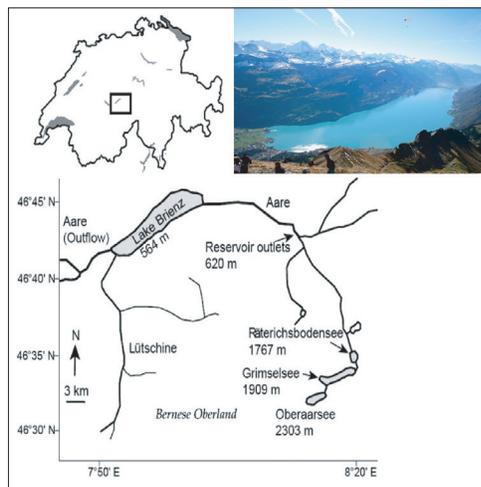
ticles. The organics of cluster 1 show a relatively high aliphatic/aromatic ratio with lower amounts of oxygen-containing functional groups, whereas the areas of cluster 2 are highly enriched in carboxyl/carbonyl-type groups. The cluster analysis and high-resolution C1s ratio images (**Figure 3**) show that inorganic phases are coated by ROM, thus leading to a change in surface charge and therefore influencing colloid/particulate stability.

All organics found in a Lake Brienz sample taken at 100 m depth showed an association to potassium-rich minerals and very comparable organic functionality to the mineral-associated organic matter of the surface waters. This

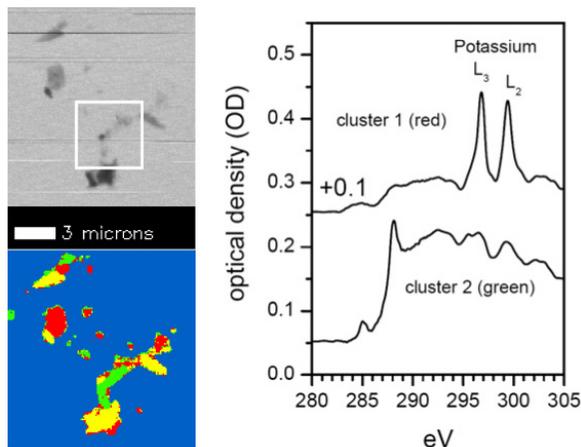
suggests that sedimentation of organic material, particularly via the association with K-rich mineral phases, is one of the major organic removal processes in the lake, thus supporting conclusions from the mass balance study. Almost pure organic material with high amounts of oxygen-containing functional groups and poor aromatic content, as found in surface waters, could not be detected in deeper zones. Taken the cluster spectra found for the Aare and Lütschine rivers as target spectra, correlation maps of organic spectral similarities for the Lake Brienz samples were calculated.  $\mu$ FTIR analyses are in general good agreement with the C1s results, although the size of the particles/colloids investigated

does not overlap due to the different resolution of the techniques used. Interestingly, the correlation maps of both methods show that the aggregate structures are built of colloidal/particulate material with spectral signatures from both tributaries at both sampling depths.

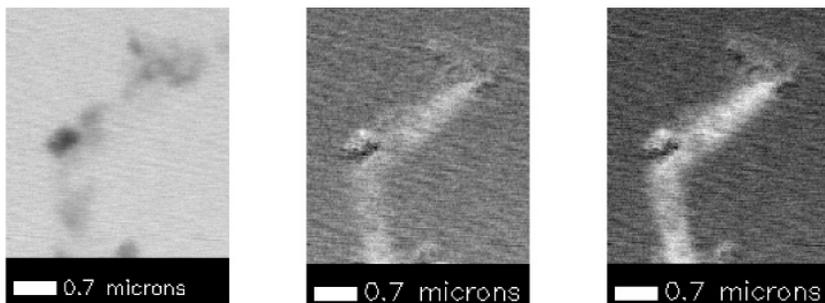
Overall, the results prove that STXM and  $\mu$ FTIR are suitable to characterize colloidal and particulate organic material and its functionality in very low organic carbon systems ( $< 0.2 \text{ mg C}\cdot\text{L}^{-1}$  ROM) and help to significantly increase the process understanding of carbon cycling in these low nutrient environments.



**Figure 1.** Map of Lake Brienz, Switzerland and its two main tributaries: River Lütschine, not affected by human activities, and River Aare, strongly modified by hydroelectric installations. Additionally inserted an image showing a view of Lake Brienz from the Rothorn summit.



**Figure 2.** Lake Brienz 1 m depth sample (July 2005). Top left: Absorption image taken at 280 eV below the C1s edge showing inorganic colloids and particles. The high-resolution ratio images shown in Figure 2 were taken in the region marked by the rectangle. Bottom left: PCA and cluster analysis of the TEM grid shows three distinctive clusters (red, yellow and green) and the background region (blue). Right: The corresponding C1s spectra of clusters red and green are shown.



**Figure 3.** Lake Brienz 1 m depth sample (July 2005). Ratio images of region marked in Figure 2. From left to right: absorption image at 280 eV, distribution of aromatics, and distribution of organics. Shades of bright grey indicate high concentrations of organic functionality.