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Rock Eval Pyrolysis : a tool for quantification of organic fluxes in present lacustrine environments

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The main objective of most organic geochemical studies performed on lake sediments is to identify the sources of sedimentary organic matter (OM). Indeed, molecular and isotopic studies allow to characterise major compositional trends between two organic poles: the one deriving from the lake production (algal and microbial OM), the other one deriving from the watershed production (contemporaneous aerial biomass and reworked OM from soil or geological formations). In order to furnish valid information on the palaeo-environmental variation and on the intensity of responsible sedimentary events (anthropogenic or climatic), it is necessary to quantify the different organic contributions and to calculate the sedimentary organic fluxes through the time.

The aim of this study is to provide a model of calculation for reconstructing the terrestrial and aquatic organic contributions delivered to a lake during the historical period (<5000 years). The model is based on a high-resolution study of a 5-metres long core sampled in the center of the Petit lac d'Annecy in the French Alps analysed by the means of Rock Eval pyrolysis. This method developed at first in the field of oil research has been successfully applied to the organic characterisation of present lacustrine sediments (i.e. Meyers and Lallier-Vergès, 1999) and is particularly adapted to high-resolution time-series studies because of its rapid and automated implementation, that requires few decigrams of sediment sample.

The approach firstly consisted of the Rock Eval analysis of the main organic sources: the terrestrial source from the watershed and the aquatic source from the lake itself. The "terrestrial pole" has been determined by analysing about twenty samples of soils (litters and organo-mineral layers), made of humus and clayey-humic substances. The characterisation of the "aquatic pole" has been realised on trap sediment samples, constituted by plankton debris and microbial-derived OM (as revealed by the petrographic observations). An average value of the CPS3/S2 and

PCS2/RC Rock Eval parameters has been defined for each organic pole. CPS3/S2 is the ratio between CO amount liberated during the pyrolysis phase (s'3 of RE6, Lafargue *et al.*, 1998) and HC (s2) whereas PCS2/RC is the ratio between RC (residual carbon burnt during the oxidation phase) and HC (s2). These preliminary results show that it is possible to obtain Rock Eval parameters typical of each major organic source delivered to the sediment. Obviously, absolute values cannot be taken as references in the sediment because many degradation processes occur between the production and the accumulation of organic matter. Concerning the aquatic OM, the present study reveals that degradation processes occurring between the epilimnion (<20 metres) and the water-sediment interface are not sufficient to alter the Rock Eval signal. Due to their natural resistant character, similar conclusions may be drawn for terrestrial OM. Moreover, many authors confirm that the main part of organic degradation occurs at the water-sediment interface that has not been studied here. The degradation state of terrestrial OM depends on the residence time of the particles into the soils before its possible storage in the flood-plain and its supply in the lake.

Despite these problems, approximations may be done to estimate the contributions of aquatic and terrestrial organic carbon in the sediment, assuming the fact that the whole sedimentary OM has been submitted to similar degradation conditions. This hypothesis is supported by the homogeneity of the sediment lithology and carbonate nature. Some lithological zones are evidenced by the colour of the sediment but are mainly induced by recurrent flood events composed by well-preserved woody fragments (Noël *et al.*, 2000). It is thus possible to estimate that the RE parameters variations are directly linked to the fluctuation between supplies of both sources and to calculate these contributions all along the core. For this, typical samples containing mostly pure lacustrine OM or terrestrial OM have been identified in the sediment and analysed by Rock Eval analysis. Their composition have been used as references in the calculation of respective parts of organic sources. The figure 1a shows the depth distribution of calculated organic sources compared with petrographic analysis of particles (1a for aquatic OM and 1b for terrestrial OM) for a low-resolution sampling. The good agreement between the two methods shows that Rock Eval results may be used for characterising organic sources at higher-resolution (at the millimetric scale). The palaeoenvironmental interpretation of these

fluctuations underlines the double impact of human activity and climate on both the watershed runoff and the lake production. The discrimination between these two factors is still in course.

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