Sequential extraction and EXAFS measurements on Fe and S mineral phases in lake sediments

M. Bott   ETH-EAWAG, Seestr. 79, CH-6047 Kastanienbaum, Switzerland

L. Spadini   LGIT-IRIGM, BP53, Université Grenoble I, France
A. Manceau

B. Wehrli   ETH-EAWAG, Seestr. 79, CH-6047 Kastanienbaum, Switzerland

The aim of this work is to check whether redox sensitive compounds in a chosen eutrophic lake sediment store information about palaeoclimatic data. Climate parameters like cold winter temperatures and strong winds are able to mix the lake. As a consequence oxygen comes in direct contact with the sediment-water interface. As iron(II) is highly sensitive towards oxidation in presence of oxygen and iron(III) is a good electron acceptor under anoxic conditions the iron cycle is strongly influenced by hypolimnetic redox conditions. For this study sequential extraction techniques were applied as well as EXAFS spectroscopy on the iron K edge. The history of eutrophication was reconstructed by Niessen *et al.* (1987). The concentration of oxygen in the bottom water of Lake Baldegg from 1950 to 1993 was published in Wehrli *et al.* (1997).

High resolution sequential extraction of iron sulphides. Fresh sediment samples were taken from the deepest site of the highly eutrophic Lake Baldegg (Switzerland). The cores were airtightly closed and transported to the laboratory. 5 mm segments of the fresh material were sampled in a glove box without any further treatment. Acid volatile sulphide (AVS), chromium reducible sulphur (CRS), total iron and total sulphur were determined. Important for this work was the sediment dating. The dry weight of the fresh samples were correlated with the data available from a exactly dated reference freeze-core (Lotter *et al.,* 1997). A precision of better than two years could be reached with this method.

Results. The total iron concentration exceeds the total sulphur concentration. Thus the lake sediments are not iron limited. A high correlation of the AVS data (iron sulphides) with average air temperatures was found in the highly eutrophic part from 1950 and 1982 of the sediment. In addition the CRS (pyrite) data show a negative correlation during this time (Fig. 1). Thus AVS and CRS data in our system correlate with climate parameters. In the eutrophic part of the sediment the AVS concentration contri-

butes to about 50% of the total iron. Older sediment has a much smaller AVS concentration. The black colour of the sediment correlates directly with the AVS data. Total iron shows a very constant profile. A slight decrease in its concentration is due to eutrophication. Since the lake is highly eutrophic, dissolved iron(II) is transferred from the anoxic hypolimnion to the outflow. In our system AVS and total sulphur correlate well. More than 60% of total sulphur is AVS. Anoxic conditions and sulphate reduction are responsible for a high total sulphur content in the sediment. In the sediments of the mesotrophic lake the total sulphur concentration was one order of magnitude smaller than in recent sediments. Pyrite contributes only about 3% to the total iron and 5% to total sulphur.

The most interesting topic is the correlation between AVS, CRS and temperature. When the bottom waters of the lake are anoxic the sulphate reduction rate determines the sulphide concentration in the sediment. This concentration decrease when the hypolimnium becomes oxic. This situation occurs only
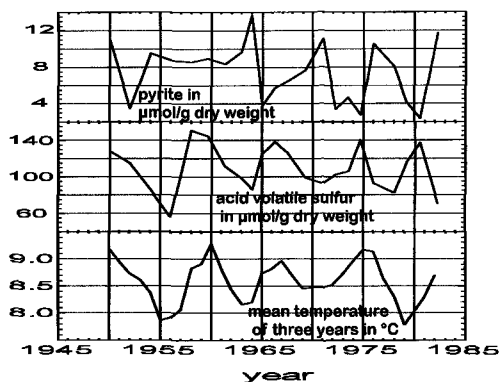

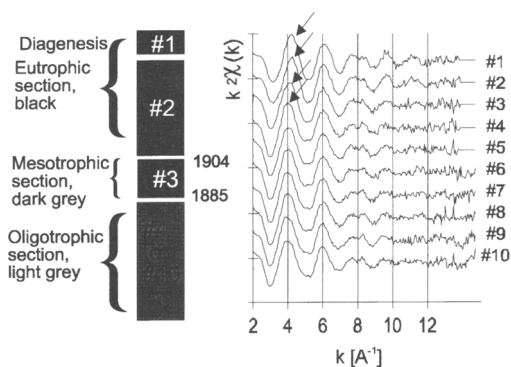FIG. 1. Pyrite, AVS concentration and correlation with the average three year temperature.

FIG. 2. Trophic regimes of the sediment core and experimental $k^2\chi(k)$ spectra. Arrows point the the phase shift difference which correlates with the trophic state of the lake.

FIG. 3. Least square map resulting from the regression analysis of #8 with the indicated pairs of reference compounds.

during cold winters when oxygen comes in contact with the sediment at the deepest site of Lake Baldegg. Under these conditions the sulphide concentration decreases due to oxidation by oxygen and a larger penetration depth of sulphate. Therefore a decreased sulphide formation results. On the other hand oxidized sulphur species enhance pyrite formation.

EXAFS spectra analysis. Measurements were performed at the L.U.R.E synchrotron facility in Paris-Orsay, France. To prevent oxidation and recristallisation of the sediment material, a fresh sediment core was sampled in a glove box during the run session, and the sediments material packed in specific air-tighten vessels. Both the eutrophic (#1 to #3) and the oligotrophic (#4 to #10) horizons were sampled and analysed by Fe K-EXAFS fluorescence spectroscopy (Fig. 2). The $k^2\chi(k)$ spectra for the 10 samples have a similar phase pattern regardless of the trophic state of the sediment which suggests the presence of a unique mineral compound. Beside this general spectral likeness, a small but significant phase shift ingoing from the eutrophic to the oligotrophic samples can be observed (Fig. 2, arrows) indicating the presence of one or several redox sensitive compounds. To identify the nature of the Fe containing minerals, each of the $k^2\chi(k)$ spectra were compared to linear combinations of reference compound spectra by least squares regression analysis. The reference database included the most
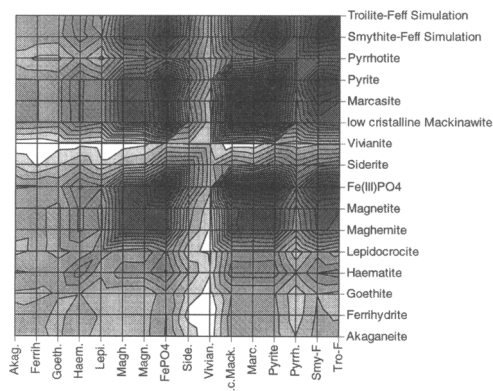
abundant Fe-sulphide, -oxide, -phosphate and -carbonate minerals. The results are presented as threedimensional map of merits of spectral decomposition in two reference components. This mapping technique allows us to evaluate various contributions and infer the nature of the predominant Fe minerals. The map of #8 is given as example in Fig. 3. White and light grey grid intersections correspond to best mathematical solutions whereas dark zones present unlikely mineral combinations. We found that the maps strongly depend on the trophic state of the sediment: All maps of the oligotrophic regime look very similar to that of #8. In this regime all mineral combinations including vivianite $Fe_3(PO_4)_2$ have a good spectral agreement. This does also account for most combinations which include iron oxides. In this respect, a particularly good agreement is found for the combination lepidocrite - siderite as reference materials. Thus, vivianite, iron oxides and siderite are the most likely predominant Fe bearing mineral compounds in this trophic regime. The situation is strongly different in the eutrophic regime (#1 and #2) where the best spectral agreements are obtained for combinations of poorly crystallized mackinawite with vivianite, pyrrhotite, goethite or marcasite spectra. In these four combinations, mackinawite has always the dominant spectral contribution. Thus mackinawite is likely to be a major Fe bearing phase in the eutrophic regime. Il will be further shown that the mapping technique allows to follow the impact of artificial aeration in the lake bottom water.