4.3. ANALYSIS OF MAIN SEDIMENT COMPONENTS

Bogumił Wicik

For quantitative analysis of the main sediment components along the whole profile a few simple standard methods were used. These methods provide proxies rather than direct estimates for the concentrations of particular components. Nevertheless, they were useful for some interpretations given in subsequent chapters.

As the proxy for organic matter content, loss on ignition (LOI) was used. Loss on ignition is defined as a loss of sample mass after heating to 550°C, with respect to the mass of sample dried to 120°C. The content of calcium carbonate was determined by simple Scheibler method. Such an approach seems justified as the carbonates in the Lake Gościąż sediments consist almost entirely of calcite (Łącka et al., Chapters 7.3 and 8.2). The amount of iron in the sediments was measured by the iodometric method, and it was displayed in the form of Fe_2O_3 content.

4.4. STABLE ISOTOPE ANALYSIS

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The samples of the core material 0.5 to 1.0 cm^3 in volume collected for stable-isotope analyses were sealed in plastic vials and transported to the laboratory, where they were dried (12 hours, +90°C), ground to a fine powder, homogenized, and stored in tightly closed plastic vials. A portion between 60 and 120 mg was used for individual analysis, depending on carbonate content in a given core. Chosen samples were analysed twice. Decomposition of carbonates to gaseous CO_2 and phosphates for isotopic measurement was done by the standard procedure (McCrea 1950) at controlled temperature and pressure. The analyses were performed using the Micromass 602C mass spectrometer equipped with computer data output.

The results are reported as per mille deviations of $^{18}O/^{16}O$ ($^{13}C/^{12}C$) isotopic ratios in the analysed carbonates from those in the PDB carbonate standard, following the generally accepted notation (Craig 1957):

$$\delta^{18}O = \left\{ \frac{(^{18}O/^{16}O)_{\text{sample}}}{(^{18}O/^{16}O)_{\text{standard}}} - 1 \right\} \times 1000‰$$

$\delta^{13}C$ – analogous definition.

The overall analytical uncertainty of the isotope analyses (one sigma for single measurement) was around 0.2‰ for $\delta^{18}O$ and 0.1‰ for $\delta^{13}C$.

4.5. MINERALOGICAL AND GEOCHEMICAL METHODS

Bożena Łącka & Ewa Starnawska

Mineral composition of sediment samples was determined by X-ray diffraction (XRD) and differential thermal analysis (DTA). The morphology and chemical composition of individual mineral phases as well as the variation in the structure and composition of the varve sequences were investigated with scanning electron microscope (SEM) and energy dispersive spectrometry (EDS).

Every sample was air-dried and ground in an agate mortar to 200 mesh size for XRD, DTA, and chemical analysis.

The diffractograms of untreated samples were recorded by the reflection method, using quartz-filtered CuKα radiation (Sigma 2040). For the very small samples, the XRD transmission method was applied with the INEL position goniometer. In both cases the INEL computer registration programs were used. The fluorescence from high concentration of amorphous Mn and Fe hydroxides excluded the detection of minor and poorly crystallized mineral components of the sediments.

DTA was performed in air on 200 mg samples with Al_2O_3 as a standard (MOM, type Q1500D). The samples were heated 10°C/min. up to 1000°C. The sensitivity of TG determination was 10 mg over the whole temperature range. In addition to mineral identification, the carbonate carbon was determined from the weight loss between 550 and 1000°C (the temperature range of carbonate decomposition). CO_2 content recorded in this way was recalculated to determine semiquantitative content of carbonate minerals. However, for the Mn-rich samples the CO_2 concentrations were too low even to fix the total Ca with calcite. This incompatibility of the Ca and CO_2 content is probably caused by the gain in weight due to the oxidation of Mn and Fe species during the ignition. Comparison of the calcite content calculated from loss on ignition between 550 and 1000°C (Wicik, Chapter 3.4) and from the Ca content (Fig. 4.3) shows that the first values are slightly lower than those calculated from total Ca content reduced by the value corresponding to the gypsum content in sediments.

The samples for SEM examination were air-dried, and damage of delicate sediment structure as well as of neoformed minerals could have taken place. In all cases, the chipped fragments of the core were mounted perpendicularly to the varve succession and coated with carbon and then with gold. SEM examination was performed with JSM 840A microscope (JEOL). The qualitative chemical analyses of minerals and varves were carried out by AN 10000/85S EDS (Link) in the 2000 μm^2 microarea and, in special cases, in the spot mode.

Some of samples were chosen for acid-dissolved frac-

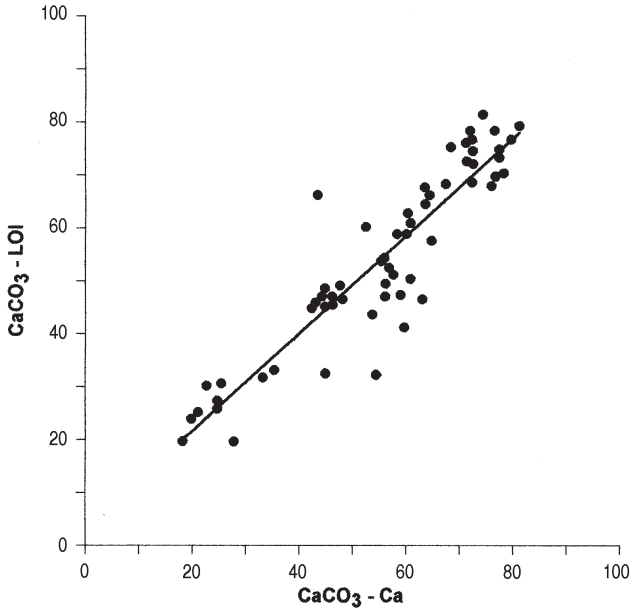

Fig. 4.3. Comparison of calcite content calculated from LOI and from Ca concentration. r = 0.92, y = 6.21 + 0.96·x.

tion analyses. Other bulk samples were taken into solution by the mixture of nitric and hydrofluoric acids. For samples treated by the latter procedure, major elements (Ca, Mg, Mn, Fe, Al, Ti) and minor ones (Zn, Cu, Cr, Ni, Sr, and Ba) were determined by means of a Perkin Elmer atomic absorption spectrometer (AAS). Cr, Ni, and Cu concentrations were close to the detection limits of these elements in the method applied: Cr ≤10 ppm, Ni≤ 10 ppm, Cu≤ 5 ppm. The fluorescence caused by high concentration of Mn prevented the precise determination of Ti content. The concentrations of K and Na were analysed by optical flame emission spectrophotometry.

For determination of biogenic SiO_2,, separate portions of the sediments were dissolved in 5% Na_2CO_3 solution and analyzed by the colorimetric method. Concentrations of P and total S were analyzed also from separate portions of the sediment after their dissolution with *aqua regia*. S and P contents were determined by gravimetric methods.

Total carbon content was determined with a LECO carbon analyser, and the content of organic carbon was estimated from the difference between the total carbon and carbonate carbon concentration calculated from the TG curves. But, as mentioned above, the carbonate carbon concentrations probably are correct only for samples poor in Mn and Fe.

For 25 samples the analysis of organic material was performed on the Perkin Elmer elemental CHN analyser.

Similar analytical procedures were used for element-content determination in 1M HCl dissolved sediment fraction. Mg, Mn, Fe, Sr, Cu, Zn, Ni, and Al concentrations were determined by AAS, and sulphate-sulphur by the gravimetric method. Because of the rather high Ca content within all samples, the EDTA titration method for its determination was applied.

4.6. PALAEOBOTANICAL ANALYSES

4.6.1. Palynological analysis (pollen and extra-palynomorphs)

Magdalena Ralska-Jasiewiczowa & Bas van Geel

The samples used for analysis of pollen and other plant microfossils were of two different volumes: samples of 1 cm^2 per known number of laminae couplets in the case of annually laminated sediments, or samples of 1 cm^3 volume in case of other sediment types (see Ralska-Jasiewiczowa et al., Chapter 4.1.3).

The reference profile G1/87 was mostly subsampled with the routine 50 yr time resolution, with samples embracing 10 couplets, except for the bottom part, where samples of 6-couplets were collected and analysed with a denser time resolution, and the upper 6 m, where the subsampling intervals were not quite regular due to the lamination disturbances. At the contacts between subsequent sediment segments (of 2 m), where the continuity of lamination was slightly destroyed, the subsampling was completed from a twin core G2/87. This core was divided into segments at different depths and correlated precisely with G1/87 by "year-to-year" laminae analysis (Goslar, Chapter 6.1).

The other profiles were subsampled with 10-couplets samples but with varying time resolution for laminated sediments (G1/90, T1/90 – Late-Glacial part), and for non-laminated sediments with 1 cm^3 samples, either continuously (G1/90-bottom part), or in intervals of 10 cm, 5 cm, and smaller intervals (G28/92 and T1/90 – Holocene part).

The chemical preparation of samples was based on the Faegri & Iversen (1975) acetolysis method with two different ways of pre-treatment: gravity separation of organic and mineral matter by heavy-liquid mixture of bromoform and alcohol (specific gravity 2) was applied to the samples from G1/87 profile prepared at the Hugo de Vries Laboratory of the Amsterdam University; the samples from all other profiles prepared at the Palaeobotanical Department of the Institute of Botany in Cracow were pre-treated with cool HF and HCl to remove mineral matter and carbonates.

One to four *Lycopodium* pellets containing 13,500; 12,077; 11,300±400 or 10,850±200 *Lycopodium* spores were added to all samples to enable the calculation of pollen concentration according to the method of Stockmarr (1971, 1973). The samples were embedded in pure glycerine, and no staining was applied.

The pollen counts of samples from profile G1/87 and from the frozen cores (GF) were performed by two persons separately on each sample using the same sample