ment. The G1/90 core was taken in summer from a raft. The shifting of the raft during the penetration of hard sediment caused the consecutive segments to be taken from slightly different locations, and a mistake in the control of the coring depth could be the reason for the overlap (Więckowski, oral inf.).

The photograph in Fig. 7.11 illustrates the correlation of laminated sequences in western deep with those below and above the sand layer in the central deep. In spite of the distinct difference in sedimentation rates, the correlation above the sandy layer is quite clear. Below it the similarity of the varved sequences is weaker, and with no support from additional data the correlation could not be defended. The close similarity of δ^{13} C and δ^{18} O curves in fragments of both cores (Goslar et al. 1993, see Kuc et al., Chapter 7.6) and of AL/YD transitions reflected in pollen spectra (Ralska-Jasiewiczowa et al., Chapter 7.4), however, strongly confirms the proposed correlation. According to the present status of correlation, the sandy layer corresponds to the period of only 4^{+6}_{-2} yr. The quoted error reflects an uncertainty in counting the doubtful varves (similar to those described in Chapter 7.1) in the section of G1/90 corresponding to sand layer.

The continuous lamination through the whole YD is also revealed in the core T1/90. The bottommost lamination in this core is probably older than in any other cores. Unfortunately, the oldest short laminated fragment (205 varves) was found in separate 1 m segment and was not correlative with the continuous chronology.

7.3. MINERALOGY AND GEOCHEMISTRY OF THE YOUNGER DRYAS SEDIMENTS FROM LAKE GOŚCIĄŻ

Bożena Łącka, Ewa Starnawska & Michał Kuźniarski

The mineral composition of bulk homogenized Late-Glacial samples each encompassing 6 varves, is dominated by carbonates and poorly crystallized or amorphous hydroxides and oxyhydroxides of Mn. Minor admixtures of gypsum and clastic minerals were detected by XRD in every sample. The clastic mineral fraction consists of quartz, feldspars and layer silicates (mica, chlorite, and mixed-layer species). Because of the high background on the diffractograms caused by considerable high concentration and poor crystallinity of Mn phases, the precise identification of Mn minerals as well as mixed-layer silicates was impossible. Only two Mn hydroxides, pyrolusite and todorokite, were detectable by XRD.

The carbonate fraction within the uppermost part of the Late-Glacial deposits consists of at least two mineral phases: the minor component is calcite, and the other one is mostly carbonate that displays the presence of $d_{104} = 2.88-2.89$ Å reflection in the powder-diffraction patterns. This d_{104} value is one for dolomite. However, it is also

characteristic for Ca-rhodochrosite and for carbonates with chemical composition fitting to the ternary system CaCO₃ – MnCO₃ – FeCO₃ (Capobianco & Navrotsky 1987, Peacor & Essene 1987). EDS analyses of the intergrowing carbonate grains within single varves report presence of Mn, Ca, and frequently – Fe. None of analysed grains contained Mg. Moreover, DTA and TG curves of homogenized samples did not show any dolomite endothermal effect at 850°C. Thus in the case investigated the value $d_{104} = 2.88-2.89$ Å indicates Ca-rhodochrosite with about 20 mole per cent of CaCO₃ or carbonate close to the ankerite composition (Ca, Fe, Mn)(CO₃)₂. It is the main carbonate within Late-Glacial deposits.

The other minor carbonate phases display in diffraction patterns d_{104} values of about 2.96 and 2.80 Å, corresponding to Ca-kutnahorite (Bini & Manchetti 1985, Cancian & Princivalle 1991) and siderite, respectively. Occurrence of these two Ca- and Mn- bearing carbonates and in one sample also rhodochrosite, may arise from the metastability of the carbonate system within the deposits.

In the diffraction patterns of raw powdered and homogenized samples only the mineral phases described above were recorded. However, Pawlikowski (1990) reported the presence of manganese sulphides – alabandite and hauerite – within the deposits underlying the Younger Dryas sequence.

The results of chemical analyses of bulk homogenized samples encompassing 6 varves are plotted versus calendar years BP (Fig. 7.12). Usually diagrams of element concentration show the general pattern of changes of sedimentation and diagenesis conditions. In continental environments both of them are strongly influenced by climate variations.

The Younger Dryas deposits in Lake Gościąż are distinguishable by their high concentration of Mn (Fig. 7.12). The uppermost sediments of the core investigated from the central part of Lake Gościąż contain up to 12 weight per cent of Mn. The Mn content of the underlying deposit is even higher, up to 20 weight per cent (Pawlikowski 1990) – as high as in the Mn-ores.

The Fe content (Fig. 7.12, about 4–5 weight per cent) is lower than Mn concentration, and the value of the Mn/Fe ratio (2.5–3.5) exceeds by two orders of magnitude the mean Mn/Fe ratio for shales (Perelmann 1977). The processes controlling the mobility and distribution of Mn and Fe in sedimentary environments depend on the factors causing the decrease of redox potential and/or the increase of acidity (Balistrieri et al. 1992, 1994, Søresen & Jørgensen 1987, Young & Harrey 1992). Because Mn solubility exceeds that of Fe, for any given Eh and pH value, the separation of these elements occurs during soil formation processes, lacustrine deposition, or diagenesis of lacustrine sediments (Borchert 1970, Crerar et al. 1971/72). Soil-formation processes due to mineralization of organic matter create acidic-reducing conditions with-



Fig. 7.12. Plots of Mn, Fe percentages and Al, K, and Na sum versus calendar years BP for the Younger Dryas samples from the Lake Gościąż core G1/87. The plots for early and mid-Holocene are shown for comparison.



Fig. 7.13. Manganese mobility in generalized tundra and podsol soil profile and Mn accumulation during oligotrophic and mesotrophic stages of lacustrine deposition (after Crerar et al. 1971/72 and Borchert 1970, modified).

LAKE GOŚCIĄŻ



Fig. 7.14. Plots of Ca and Mg, biogenic silica, phosphorus, organic carbon percentages and parts per million of Sr versus calendar years BP for the Younger Dryas samples from the Lake Gościąż core G1/87. The plots for early and mid-Holocene are shown for comparison.

in the soil. Negligible thickness of C_{org} -rich soil horizon in subarctic climatic zone favours rapid oxidation and immobilization of Fe just below this horizon (Fig. 7.13). In contrast to Fe, the soluble Mn organic and inorganic complexes as well as Mn²⁺ adsorbed on organic and inorganic particulate matter could be transported away by groundwaters and precipitated in environments with redox conditions suitable for Mn oxidation. Mn ores are frequently formed in lakes during the oligotrophic stage of the lacustrine evolution in tundra regions (Crerar et al. 1971/72).

Another process of the appreciable Mn-enrichment of lacustrine deposits takes place when anoxic sediments are in contact with the oxic bottom waters. Mn mobilized within anoxic sediment may be transported horizontally towards the lake center due to diffusion (Schaller & Wehrli 1994). Thus the Mn concentration within the central part of such a lake is far greater than the one to be controlled by the tundra soil-formation processes only.

The changes in the contribution of clastic material to the sediments are represented by the variation of Al, K, Na, and Mg concentration (Fig. 7.12). All these elements are mainly present in the aluminosilicate minerals and for the investigated sediments show the same patterns of distribution with time. The very low contents of Al, K, Na, and Mg progressively decrease from the bottom to the top of the part of the section considered. Moreover, the thorough SEM examination did not reveal any evidence for such a negligible portion of clastic fraction. Thus it seems that the clastics are enclosed inside carbonate aggregates.

Like Mn and Fe, the concentration of calcium does not exhibit any considerable variation along the uppermost section of the Younger Dryas deposits (Fig. 7.14). A very similar distribution patterns of Ca and Sr indicate a tight relationship of Sr to Ca-containing carbonates, which are the main mineral phases of Ca.

The content of biogenic silica, phosphorus, and organic carbon reflect the biogenic productivity of the lake system (Fig. 7.14). The distribution patterns of these elements with time could be used to define the eutrophication stage of the lake. The content of biogenic silica in the sediments deposited between 12,239–11,608 cal BP is extremely high (4–10 weight per cent), with two concentration maxima at 12,045–11,997 and 11,802–11,751 cal BP. In contrast to biogenic SiO₂, the content of phosphorus is low and changes in the narrow range of 0.3–0.4 weight per cent. In the distribution pattern of this element only one concentration maximum is marked around 12,045 cal BP.

These changes of mineral and chemical composition versus time reflect only the general pattern of variation in the lake environment during consecutive six-year periods of deposition. The nature of annual sedimentation and short-term seasonal variation of the physical and chemical parameters in water and sediment column should be reconstructed from the composition and microtexture of a single varve. The fragments of varved sequences from the uppermost part of the Younger Dryas deposits examined under SEM show that they consist of distinctly differentiated carbonate laminae alternating with laminae containing well preserved diatom frustules (Fig. 7.15A). Within annual succession of the varves the predominance of different diatom genera was observed (Fig. 7.15B). These sharp differentiations were not visible within the youngest Younger Dryas samples (about 11,751 cal BP) because of the dense carbonate cementation within the diatom-rich layers.

The carbonate minerals occur in irregularly shaped grains within all the above-mentioned types of laminae. Carbonate aggregates occurring in porous and thick laminae usually consist of intergrowing smaller crystals (1–2 μ m in diameter). The grain and crystal surfaces are rounded and rough, probably due to the Mn hydroxides and oxides coatings (Fig. 7.15C).

Within a few of Mn-enriched laminae scarce single and multiply nucleated barite crystals were identified by EDS. The disk-like shape of the barite crystals suggests the supersaturation of pore water with respect to barite and/or high concentration of ions, as well as organic and inorganic complexes in pore water (Shikazano 1994).

The Younger Dryas deposits from the central part of Lake Gościąż should be classified as Mn ores. The minor admixture of terrigenous material eliminate a great influx of clastic material by surface inflow, so it cannot be the source of Mn. Hence the manganese within the lake water column could mainly be derived from the groundwater. The very high Mn/Fe ratio in the Younger Dryas deposits of Lake Gościąż, up to 3.5, probably results from the separation of these elements in the subarctic weathering zone followed by the transportation in groundwaters and deposition in the oligotrophic lake. The lack of chemical data for nearshore sediments does not allow us to verify the possibility of Mn enrichment arising from the horizontal diffusion towards the central part of the lake. Processes involving the mobilization of Mn during the early diagenesis of sediments are presumably of minor importance. Mn and Fe separation is observed in microscale within a single varve, in which the carbonate layer is divided into two parts: one is enriched in iron and the other one in manganese. However, such a process could not cause any increase of the total content of manganese up to 20 weight per cent.

The annual rhythmic sequence of varves comprising almost solely frustules of diatom genera and almost pure carbonate with Mn and Fe hydroxides indicate that the flux of particulate matter was seasonally differentiated, the bottom current activity was minimal or absent, and the decay of organic matter was not intense enough to produce much gas (Kelts & Hsü 1978). All these parame-



Fig. 7.15. A – SEM photograph of core slice of varved sediment. Thick laminae produced by diatoms blooms are periodically interlayered with thin laminae of carbonates. Bar scale = $100 \mu m$. B – SEM photograph of white lamina consist of subsequential, seasonal diatom layers of various genera. Bar scale = $10 \mu m$. C – SEM photograph of beige lamina showing fine crystals and aggregates of carbonates. The barite twins visible at the arrow mark. Bar scale = $10 \mu m$. D – EDS spectrum of the carbonate layer. Carbonate aggregates are enriched in Mn and contain small admixture of Fe and traces of Ba.

ters as well as the Mn enrichment suggest an oligotrophic stage of the lake evolution during the Younger Dryas.

7.4. LATE-GLACIAL VEGETATION HISTORY RECORDED IN THE LAKE GOŚCIĄŻ SEDIMENTS

Magdalena Ralska-Jasiewiczowa, Dieter Demske & Bas van Geel

This chapter presents the development of Late-Glacial vegetation in the NW part of the Gostynińskie Lake District in central Poland. The lakeland is located on the western side of Vistula valley in its middle course, in the depression called Plock Basin, which was filled by the southernmost ice lobe during the maximum extent of the Vistulian Glaciation (Churski, Chapter 2.1).

The reconstruction of vegetation history is based on palynological and partly also on plant-macrofossil investigations of the Lake Gościąż sediments. The annual lamination of these sediments covers altogether nearly 13,000 yr (Ralska-Jasiewiczowa et al. 1987, Goslar, Chapters 6, 7.2). The best developed laminae occur in the deepest parts of the lake, but they reach only as far back as the latter part of the Late-Glacial. The records of ear-