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Preliminary investigation of mineralogy and chemistry of peats from the Kietrz site, southern Poland

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Abstract

Peat bog deposits provide a very important record of past environmental conditions, preserving biotic and abiotic processes that occurred in the vicinity of the bog. In this study, we examined three peat bog profiles from Kietrz, located in the micro-region of the Głubczycki Plateau, southern Poland.

The objective of this study was to determine the type of peat occurring in this area, through examination of its mineral composition, and evaluation of the total carbon and total sulphur content. In addition, we measured peat reaction (pH) and identified floral and faunal components occurring within the peat deposits.

The peat comprises primarily of fragments of fossilized plant and mollusk remains, as well as minerals (calcium sulphates, calcium carbonates, and pyrites). Additionally, an assemblage of iron oxides/hydroxides, K-feldspar, apatite, zircon, and quartz grains was identified. A neutral and/or light alkalinity was recorded for the peat deposits, but an increase in acidity (pH) with increasing depth through each peat profile was also recorded. We observed a positive correlation between the pH and chemical composition of deposits, where a significant presence of calcite is associated with higher reaction (higher pH), whilst a lower pH is characteristic for sediments where carbonates are rare. The recognized species of mollusks are typical of shallow, fresh-water stagnant reservoirs with a high fluctuation of water level.

Key words: peat, mineralogy, scanning electron microscope (SEM), pH, total sulphur (TS), carbon content (CC)

Introduction

Peat swamps are recognized as important biogenic, geological deposits, formed through sedimentary processes (Borówka et al., 2014). The formation of peat deposits is characterized by a lack of oxygen and highly hydrated conditions, and such environmental conditions contribute to plant decomposition and afterwards to various biochemical changes within the deposit. Depending on the hydrological conditions of peat bogs, biogenic deposits can be characterized by a diverse

lithogeochemistry (Domińczak and Okupny, 2010). Organic matter sedimentation is driven by processes such as an increase in supply of allochthonous mineral matter and adsorption of dissolved water ions by clay minerals, which contribute to the chemical composition of organic sediments (Borówka, 2007). The chemical composition of peat organic matter is characterized by a complex mixture of organic compounds, which may include organic acids and their salts, bitumens, cellulose, lignins and proteins (Tobolski, 2000). All of these organic compounds undergo biochemical

transformations, which may lead to the formation of calcium carbonate (CaCO_3), Fe-rich carbonates (FeCO_3), and iron hydroxides (FeOOH , meadow ore). Organic matter decomposition often takes place in anaerobic conditions, where released hydrogen sulphide enables the precipitation of iron sulphides (FeS , FeS_2). Biogenic sediments that form in continuously or periodically wet environments show changes in redox features. This is seen in wetland environments as periods of variation in iron and manganese reduction (Marcinek and Komisarek, 2011). In addition to the occurrence of other chemical compounds (e.g. secondary carbonates) in biogenic sediments, the hydrological regime and geological setting of the peat bog area are important. These factors affect peat type, decomposition rate, and the intensity and direction of

transformations, which take place within these deposits (Ilnicki, 2002).

This study focuses on the mineralogy of the studied peats which is considered a product of various reactions, and depend on several factors, with depth, pH, non-organic sulfur and carbon content, lithology, and water content being the most important.

Material and methods

Study area

We studied peat bog profiles from Kietrz ($50^{\circ}04'37.2''$ N, $18^{\circ}02'44''$ E), located in southern Poland, within the meso-region of the Głubczycki Plateau, formerly of the Silesia Lowland macroregion (Fig. 1). The area of peat bog lies within a region of the Głubczycki

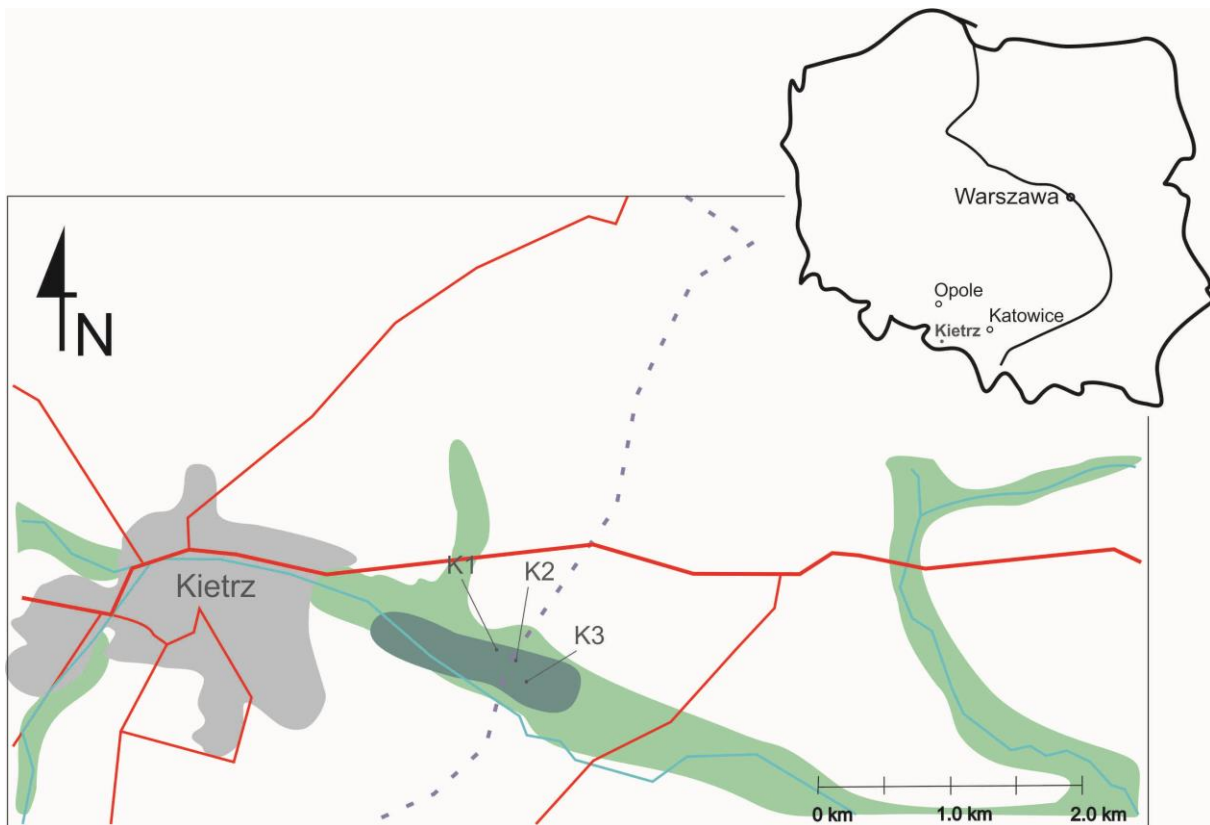


Fig.1. Location of studied peatland in Kietrz site, southern Poland. Source: Author's compilation

High Plain, where the following two secondary regional units can be distinguished: the Grab Suchej Psiny (Trzepla, 1997), a feature that rises tens of meters above surrounding valleys, with a loess cover at its apical part; the Depression of Troi comprising wide river valley, cut into a loessal high plain. The peat bog in Kietrz and others occurring in this area belong to peat bogs of Moravian Gate valley/area.

Sampling

Peat profiles were collected in 2014 from three zones of the Kietrz peat bog, consecutively K1 (1.95 m), K2 (3.50 m) and K3 (3.60 m). For this study 10 samples were investigated for profile K1, and 20 samples each for K2 and K3 profiles. Instorf (Eijkelkamp) probe was used for sample collection until the following monoliths were encountered: 14 single monoliths $0.05\text{ m} \times 0.5\text{ m}$ and one $0.05\text{ m} \times 0.4\text{ m}$. Profile K1 was located in a marginal section of the peat bog, and profiles K2 and K3 were located towards its central section (Fig. 1). The peat bog is covered by a soil layer up to 0.6 m thick and is situated within an agricultural area adjacent to the forest. According to the nomenclature of System of Spatial Information (geographic information system) regarding swamps in Poland (GIS Swamps), provided by The Institute for Land Reclamation and Grassland Farming in Falenty, the peat bog in Kietrz was assigned the number 4826009AB. It is characterized as a peat bog of the lowland type with interlayers of a high and transitional type, and with marked lacustrine phases. This kind of peat bog was further defined as bulrush-mineral.

Methods

The mineralogy of samples K1, K2, and K3 were investigated using a Philips XL30 Environmental Scanning Electron Microscope

(ESEM) with an EDAX analyzer. The analyses were carried out in a low-pressure mode (0.3 Torr). The acceleration voltage was 15 kV. Back Scattered Electron (BSE) images were collected using a Centaurus attachment with a detector resolution of 0.3 Z. EDS spectra were analysed using Philips software.

Prior to analysis peat was air-dried and desiccated for one hour at 75°C . Samples were mounted on carbon tape placed on an aluminium plate. 110 images were taken.

The total sulphur (TS) content and carbonate content (CC) were determined using an ELTRA CS-500 analyzer. Before the analysis, moisture was removed by drying the samples for 24 hours at 50°C .

After samples were dried for 5 days in 50°C , soil acidity was measured with an Elmetron CP-401 pH meter. Dried material was ground using an agate mortar and 20 grams of peat were taken from each sample.

Results

Scanning Electron Microscope (SEM) equipped with EDS

1. Gypsum

The most common mineral in all samples is gypsum ($\text{CaSO}_4 \times 2\text{H}_2\text{O}$). It forms crystals of various in sizes, ranging from 1-2 mm long (Fig. 2). Gypsum occurs as flattened and often twinned crystals (swallowtail). Many build rose-type aggregates (Fig. 2E).

2. Pyrite

The most abundant form of sulphate in all studied samples is pyrite (FeS_2). It forms crystals ranging in size from a few microns up to 30 μm in diameter (Fig. 3 A-D). Occasionally, euhedral (octahedral) pyrite crystals 10-12 μm are present (Fig. 3C). Pyrite was observed in all but one layer (1.30-1.45 m) of the K2 profile (Fig. 7.).

3. Fe-rich oxides/hydroxyl-oxides

Fe-rich oxides/hydroxyl-oxides occur as independent grains, varying in size from a few microns up to 30 μm . In some cases, Fe-rich hydroxyl-oxides appear as massive forms enclosing other minerals (e.g. gypsum; Fig. 3E-F), and as overgrowths on pyrite, or surrounding small plant fossils. A patchy structure on BSE images reflects the varying iron contents (Fig. 3D). Single automorphic crystals of oxides/hydroxyl-oxides were not found.

4. Carbonates

Carbonate content is limited to Ca-rich carbonate (calcite; CaCO_3 ; Fig. 4A-B). The calcite crystals range from 200-250 μm . Carbonates are found throughout the three studied profiles. A 15 cm long interval in the K1 profile, from 1.30 m to 1.45 m, is rich only in carbonates (Fig. 2). A few examples of small Ca-rich carbonate fragments were found (Fig. 4C), which probably are the fragments of reworked and crushed *Mollusca* shells (Fig. 4D).

5. K-feldspar

In the deepest part (3.1-3.55 m) of the K3 profile, fragments of K-feldspars were found. They are up to 10 μm long (Fig. 4E) and the EDS spectrum confirmed their composition as most likely representative of orthoclase or microcline feldspars (Fig. 4F).

6. Clay minerals

Clay minerals commonly coat the other mineral phases and/or plant remains in the peats (Fig. 5A-B). They are not long or thick enough to obtain a clear EDS spectrum due to background interference from the signal of other elements (Fig. 5E).

7. Quartz

Quartz, the most common light-mineral phase, is almost in all cases well rounded (Fig.

5C, E) with grains varying in size from ~ 50 μm to ~ 450 μm (fraction of very fine sand).

8. Zircon

Zircon (Zr) crystals in the studied peat samples are rare-and relatively small. They are not present in profiles K1 and K2 (Figs. 6 and 7) and were only found in one layer of the K3 profile (Fig. 8). Two zircon crystals measure >10 μm long, but only one crystal shows a fragmentary sharp bi-pyramidal form with an aspect ratio of 5:2 (Fig. 5D, F).

9. Apatite

Based on EDS analyses of 5 apatite fragments, all investigated apatites may be classified as fluoroapatite. The apatite grains range from 0.05 mm - 0.1 mm in length and from 0.05 mm - 0.15 mm in width (Fig. 5A, E).

pH results

The investigated peat sediments are neutral to lightly alkaline. With increasing depth peat reaction moves towards the middle-acidic range. Only in profile K3 (Fig. 8) sample #4 (2.85 m) is pH highly acidic. In profile K1 (Fig. 6) pH contents level vary from 5.31-7.46 ($\text{pH}_{\text{H}_2\text{O}}$) and 4.90-7.23 (pH_{KCl}). In profile K2 (Fig.7.) pH varies from 6.41 to 7.56 ($\text{pH}_{\text{H}_2\text{O}}$) and from 6.21 - 7.41 (pH_{KCl}). In contrast, in a point K2 of profile K3 (Fig. 8.) reaction varies from 1.88 to 7.49 ($\text{pH}_{\text{H}_2\text{O}}$) and 1.79-7.16 (pH_{KCl}).

The total sulphur (TS) and carbonate (CC) contents

Preliminary results of TS and CC show differing values. The K1 profile (Fig. 6) is characterized by TS and CC content in the range 0.94-2.74 % and 0.00-66.41 %, respectively. In the next profile (K2; Fig. 7) TS is on average 5.18%, but a single sample sample at 2.05 m shows significantly higher

TS content (~22 %) compared with other samples in profile. CC content in this profile is ranges from 0 % to 84.13 %. The K3 profile (Fig. 8) shows increasing TS content with depth, reaching a maximum of 13.99 %. The

CC content shows a wide range of values, similar to the K2 profile. There are horizons where the CC content is as low as 0.1 %, but in others the CC is up to ~68 %.

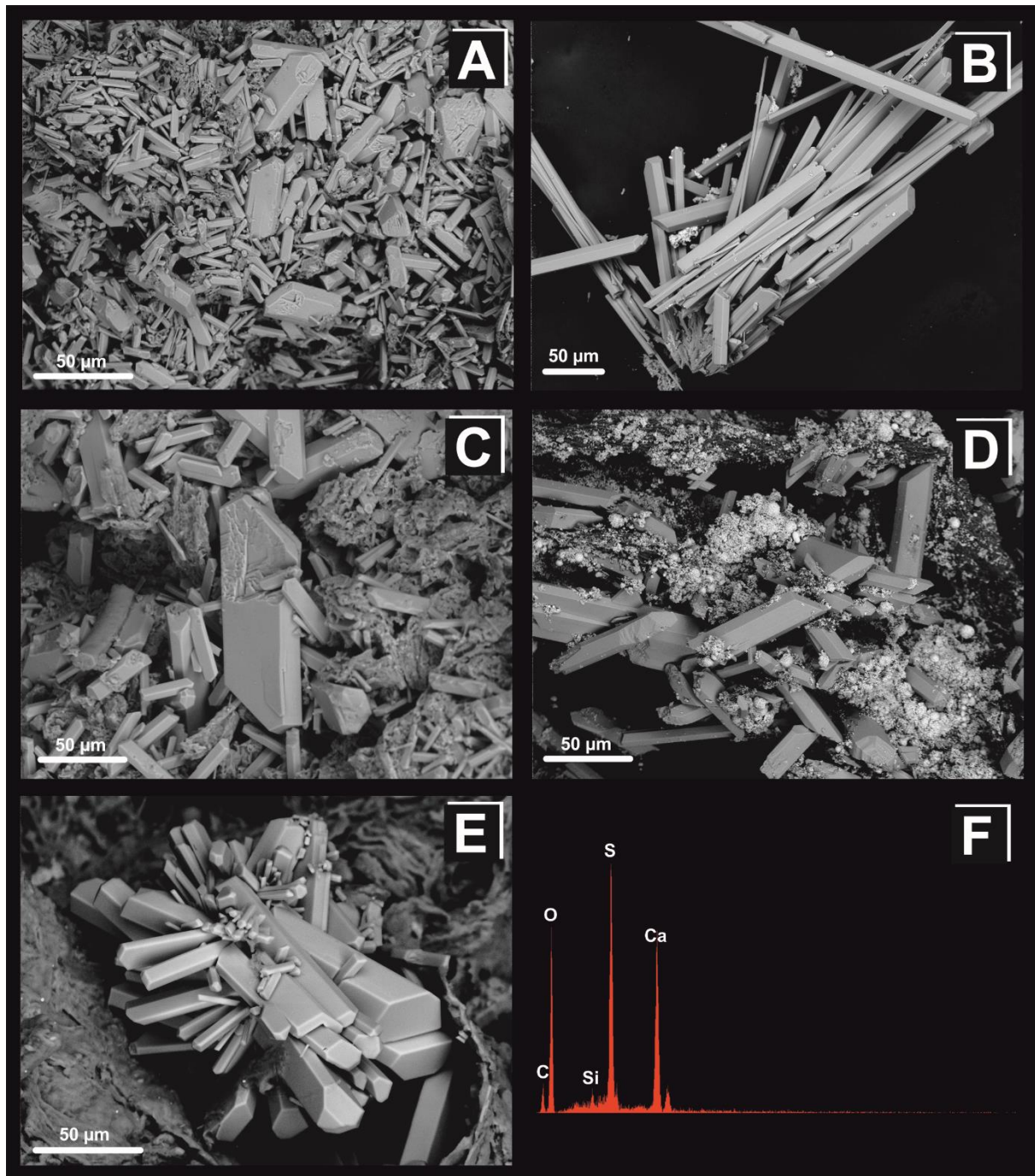


Fig.2. BSE images showing habits of gypsum crystals from peats at the Kietrz site. (A) An example of the most common type of the crystals. (B) Some crystals are strongly elongated. (C) Rarely, in some cases the crystals are partially dissolved. (D) Gypsum crystal are often associated with pyrite framboids. (E) Commonly rose-type gypsum crystals are noted. (F) A typical EDS spectrum of gypsum.

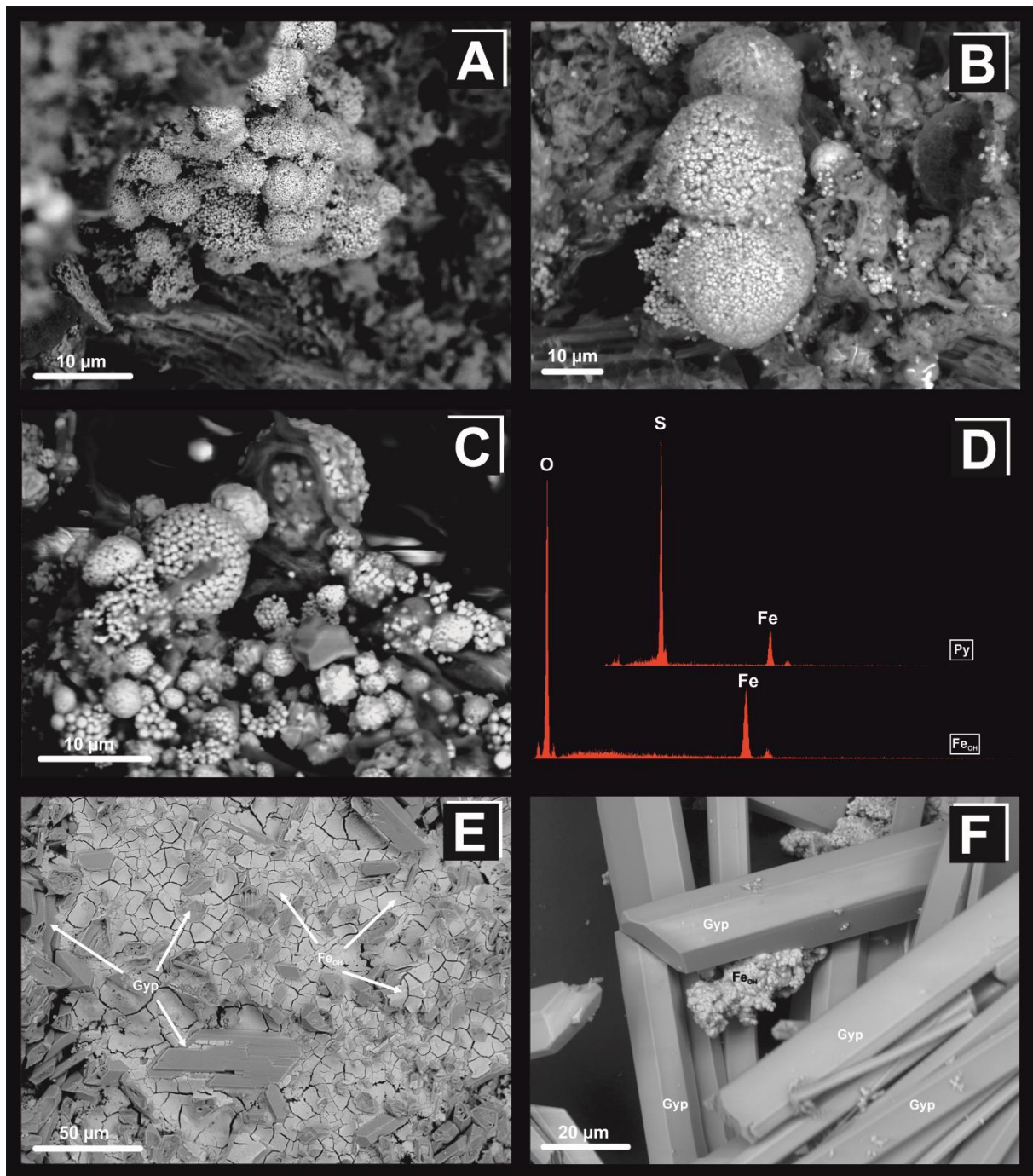


Fig.3. BSE image of pyrite and Fe-rich hydroxyl-oxides from the peats at the Kietrz site. The most common form of pyrite are framboids (A-B) which occasionally form bigger cubic crystals (C). An example of typical EDS spectrum of pyrite (Py) and Fe-rich hydroxyl-oxides (FeOX) (D). Fe-rich hydroxyl-oxides are often associated with gypsum (E) as a mass enclosing the sulphates or forming aggregates on the crystals (F).

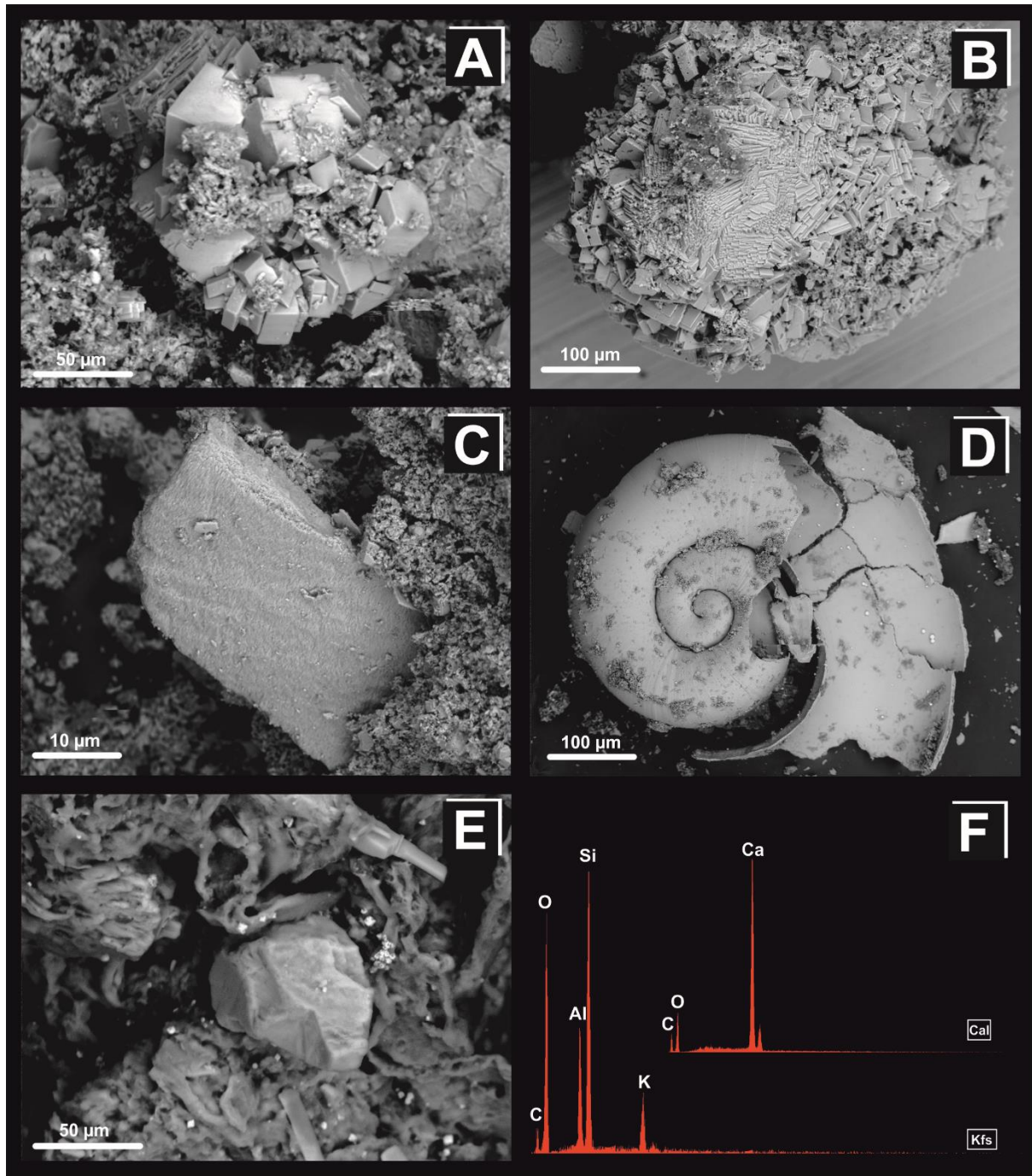


Fig.4. BSE image of calcium carbonate (calcite) (A-B), and fragmentary Mollusca shell (C-D) as well as fine-grained K-feldspar (E) from the investigated peats at the Kietrz site. A typical EDS spectrum of K-feldspar (Kfs) and (F) calcium carbonate (Cal).

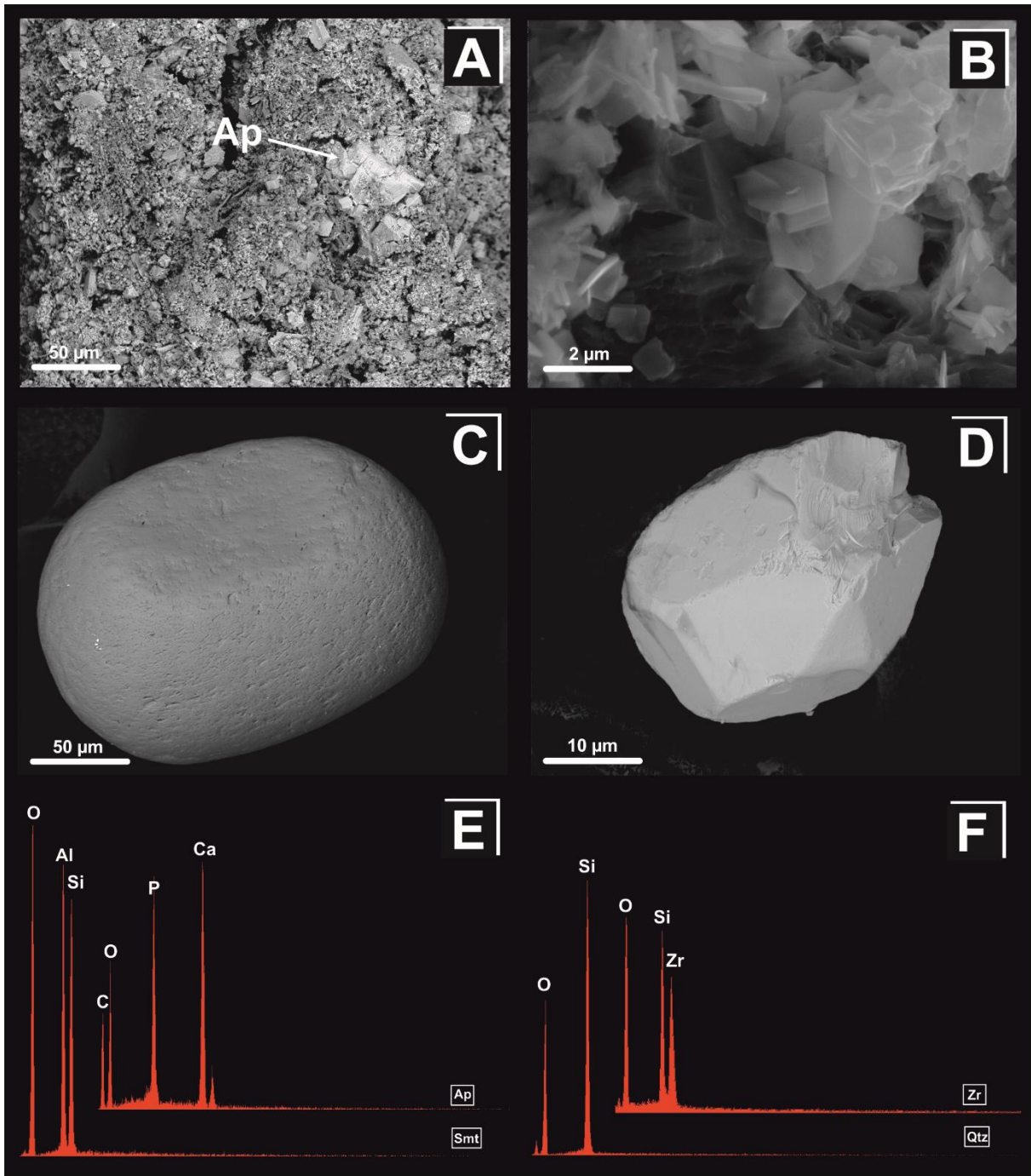


Fig.5. BSE images of rare accessory minerals found in the peats at the Kietrz Site. (A) An example of clay minerals and apatite (Ap) (B) apatite xenomorphic in shape, (C) an example of rounded quartz grain, (D) single, near-automorphic zircon crystal, (E) a typical EDS spectrum of clay minerals (Sm), apatite (Ap), (F) quartz (Qtz) and zircon (Zr).

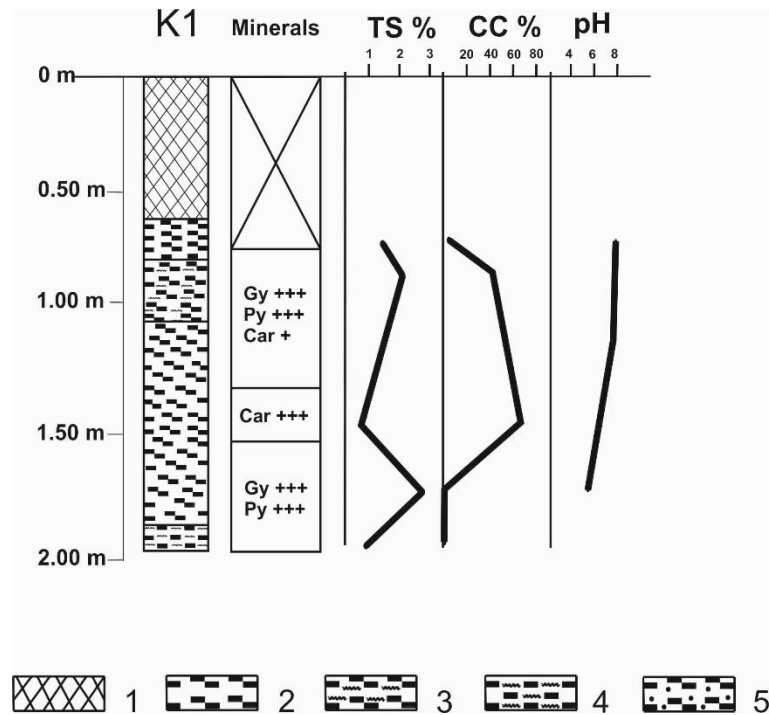


Fig.6. Relationship between lithology and contents of total sulfur (TS), total carbonate (CC), and pH_{H2O} level for samples in profile K1 (the Kietrz site). Core lithology: 1 – mineral deposits, 2 – organic deposits, 3 - organic deposit mixed with mud, 4 - mud with organic matter, 5 - organic deposit mixed with sands. Give the number to each sample in the profile on figure and reference it in text.

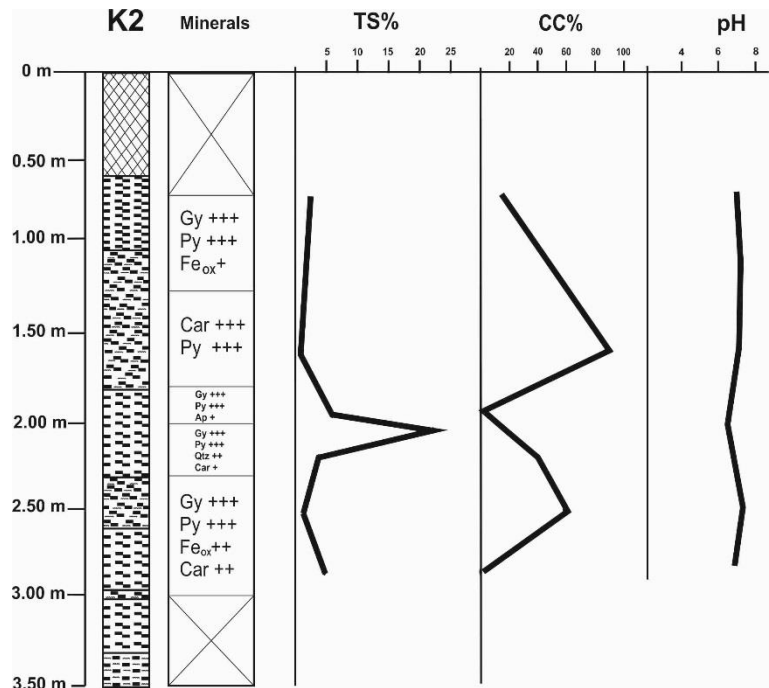


Fig.7. Relationship between lithology and same as above content, pH_{H2O} from profile K2 (the Kietrz site). The legend as on figure 6.

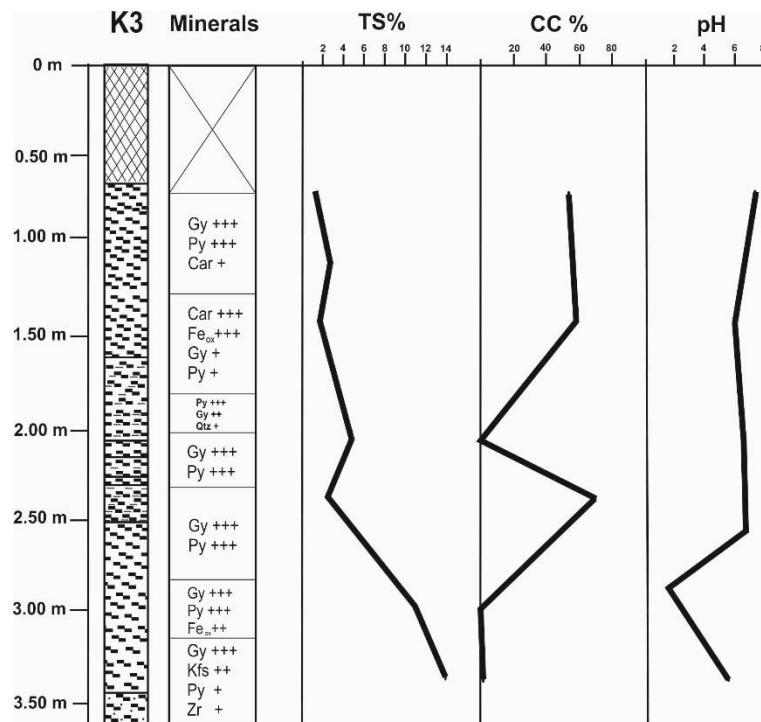


Fig.8. Relationship between lithology and same as above content, $\text{pH}_{\text{H}_2\text{O}}$ from profile K3 (the Kietrz site). The legend as on figure 6.

Discussion

In the studied peat samples, two different groups of mineral phases were distinguished: a primary "authigenic" mineral phase, with pyrite and carbonates, and a secondary mineral phase comprising gypsum, Fe-rich oxides/hydroxyl-oxides, which are products of oxidation/weathering of the primary minerals. The mineral suites and their distribution throughout the studied profiles, when compared with changing pH, TS, and CC point to differing changes in chemistry and mineralogy.

In the profile K1, three levels of gypsum and pyrite enrichment were noted. In these levels gypsum and pyrite occur up to 20 vol. %. In the lowermost and uppermost parts of this profile there are spherical aggregates of framboidal pyrites, composed of densely packed FeS_2 crystals, varying in size from a few microns up to 30 μm , and surrounded by tabular crystals of gypsum with maximum length of 500 μm . Present also are twinned, swallowtail-form gypsum crystals. In the K1

profile calcite was found at all levels except one (Fig. 6). The characteristic feature of the K1 profile is the depleted TS content in the middle of the profile, where instead CC content is enriched (Fig. 6).

The K2 profile is mainly characterized by the presence of gypsum and pyrite, with calcite at certain horizons, as well as with small amounts of quartz and Fe-rich oxides/hydroxides. In the K2 sample abundant in framboidal pyrite (5-20 μm) is seen. Pyrites (Fig. 7) occurred in the vicinity of calcium carbonates, tabular in habit, and ranging in size from 2 μm to 50 μm (Fig. 7). The largest calcite content in profile K2 is found at a depth interval from 1.3 m - 1.6 m. Iron oxides and hydroxides, gypsum and apatite were rare (Fig. 7). Very often in the studied profile regular grains of quartz (100 μm – 450 μm) were present, especially in deeper part, above 1.90 m (Fig. 7). The TS and CC contents vary throughout the profile. The largest concentrations of TS were found at a depths of 2.05 m - 2.30 m and record the highest value of TS from all three studied profiles. The CC

content varies also, but at 1.90 m the CC content was not measurable.

In the lower part of the K3 profile potassium feldspars were noted as well-formed tabular crystals of gypsum up to 350 μm (Fig. 8). Numerous framboids of iron sulphides up to 50 μm also occur. These minerals are present at the following depths: 1.3 m, 2.0-2.2 m, 2.55 m, and 3.30 m. Grains of quartz, iron oxides/hydroxides and potassium feldspars were rarely identified (Fig. 8). Calcite was identified at 1.45-1.75 m and 2.25-2.40 m, as tabular crystals ranging from 5 μm to 200 μm (Fig. 8). In this profile, near-complete and fragmentary mollusk shells and plant fragments are noted. Four samples from the K3 profile are characterized by very low CC content, that is up to 0.31 %. TS content increases with depth (Fig. 8).

Preliminary macro-remains analysis helps to distinguish several peat types, representing sedge-moss peat, sedge-reed peat, moss-sedge peat and reed peat decomposed to a various degree. Moreover, levels with organic-carbonate, organic-mineral and mineral sediments were all defined. All sediments representing the studied profiles from the Kietrz site are enriched in freshwater fauna remains (Mollusca, Cladocera).

Conclusions

Preliminary documentation of chemical diversity of biogenic sediments at the Kietrz site was determined by variable sedimentation conditions, which resulted in deposition of different types of peats. The factors partially responsible for chemical implications of the peats are geological settings and lithology of the area during peat formation.

Secondary mineral formation occurred due to chemical changes of the ground water supply connected with the peat ecosystem. Dissolution and participation of mineral phases rich in, e.g. S, C, Ca, is the main process responsible for the pH changes in the investigated peat

profiles. More detailed studies on this material should bring better characterization of organic and mineral matter evolution in the peat at this site.

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