

REPORT

1. First name and surname

Beata Smieja-Król

2. Scientific titles and degrees

2005 **PhD in Earth Sciences**, specialization geology; Faculty of Earth Sciences, University of Silesia, Sosnowiec; thesis title: *Application of Oxyreactive Thermal Analysis in the study of uraniumiferous organic matter*, supervised by prof. Janusz Janeczek.

1999 **Master of Science in Geology**, specialization: geochemistry, mineralogy, petrography; Faculty of Earth Sciences, University of Silesia, Sosnowiec; thesis title: *The Oxyreactive Thermal Analysis of Proterozoic organic matter from the natural nuclear fission reactors in Gabon*; supervised by prof. Janusz Janeczek.

3. Information on employment in scientific institutions

2006 – present Assistant Professor at the Faculty of Earth Sciences of the University of Silesia in Katowice,

2003 – 2006 Assistant at the Faculty of Earth Sciences of the University of Silesia in Katowice,

4. Scientific achievement (according to art. 16 ust. 2 from 14 march 2003 – Journal of Laws No. 65, item 595 with amendments)

- a) Title of the scientific achievement

The role of mineral components in the cycling of potentially toxic elements (PTE) in peatlands receiving pollutants from atmospheric deposition

b) Publications which constitute the achievement (with the impact factor of the journal and the number of points given by MNiSW in the year of publication)

- [1] **SMIEJA-KRÓL B.**, FIAŁKIEWICZ-KOZIEŁ B., SIKORSKI J., PALOWSKI B. (2010): Heavy metal behaviour in peat – A mineralogical perspective. *Science of the Total Environment* 408, 5924–5931.
(IF: 3,190; MNiSW: 35 points)
- [2] **SMIEJA-KRÓL B.**, FIAŁKIEWICZ-KOZIEŁ B. 2014. Quantitative determination of minerals and anthropogenic particles in some Polish peat occurrences using a novel SEM point-counting method. *Environmental Monitoring and Assessment* 186, 2573–2587.
(IF: 1,679; MNiSW: 25 points)
- [3] **SMIEJA-KRÓL B.**, JANECZEK J., WIEDERMANN J. 2014. Pseudomorphs of barite and biogenic ZnS after phyto-crystals of calcium oxalate (whewellite) in the peat layer of a poor fen. *Environmental Science and Pollution Research* 21, 7227–7233.
(IF: 2,828; MNiSW: 30 points)
- [4] **SMIEJA-KRÓL B.**, BAUERER A. 2015. Controls on trace-element concentrations in the pore waters of two Sphagnum-dominated mires in southern Poland that are heavily polluted by atmospheric deposition. *Journal of Geochemical Exploration* 151, 57–65.
(IF: 2,147; MNiSW: 30 points)
- [5] FIAŁKIEWICZ-KOZIEŁ B., **SMIEJA-KRÓL B.**, OSTROVNAYA T.M., FRONTASYEVA M., SIEMIŃSKA A., LAMENTOWICZ M. 2015. Peatland Microbial Communities as Indicators of the Extreme Atmospheric Dust Deposition. *Water Air and Soil Pollution* 226, 97 (1–7).
(IF: 1,551; MNiSW: 25 points)
- [6] **SMIEJA-KRÓL B.**, JANECZEK J., BAUERER A., THORSETH I.H. 2015. The role of authigenic sulfides in immobilization of potentially toxic metals in the Bagno Bory wetland, southern Poland. *Environmental Science and Pollution Research* 22, 15495–15505.
(IF: 2,760; MNiSW: 30 points)

- c) The description of the scientific aim, results and possible applications of the above listed publications

Peatlands, which are water-logged environments containing a layer of partially decayed plant matter (peat) thicker than 0.3 m (Ilnicki, 2002), are important in the global cycle of chemical elements, including elements which are potentially toxic (PTE) to living organisms. Due to high sorption capacity, large internal surface area, dominating anoxic conditions, the peatlands are highly capable of retaining pollutants in both dissolved and solid form. Therefore, they often act as a geochemical barriers which effectively retain potentially toxic elements (PTE) for a long period of time providing protection for natural water resources such as rivers, lakes and ground waters. Some of the PTE, like lead and mercury are retain so successfully that the changes in their concentrations in vertical profiles are used for reconstructions of air pollution through ages (e.g., Martinez-Cortizas et al., 1999; Shotyk 2002). For example, the increase of air pollution by lead during Roman Empire is easily visible in the peat profiles of lead concentrations in many European peatlands and called 'Roman peak' (e.g. De Vleeschouwer et al., 2010). The mobility of most PTE (i.e., Zn, Cd, Cu, Cr, Ni, Sb and As), although limited, depends on many factors and stays a matter of discussion (Monna et al., 2004; Rausch et al., 2005; Weiss et al., 2007; Allan et al., 2013).

The investigations of processes governing the mobility of PTE in peatlands are important also because of the danger of changing from net sinks to net sources of PTE causing water-quality deterioration, even many years after the emission of pollutants by industry is finished. Extremely high amounts of PTE are stored in peatlands located close to historical and recent centres of mining- and smelting-based industry (Jones and Hao, 1993; Nieminen et al., 2002; Linton et al. 2007). As the wetlands are developing in an uncontrolled way, the release of PTE to water is possible in unfavourable conditions of a prolonged drought, lowering of ground water level due to mine activities or a change of land use. Especially, that climate-change predictions indicate considerable changes in water balance throughout Europe and an increase in the frequency of extreme events such as droughts and high intensity rain events are predicted in the future.

In spite of many detailed investigations on the (bio)geochemistry of peatlands and the influence of different human activities on the concentrations of PTE in peat, there is a general lack of data about the role of minerals and anthropogenic particles in the behaviour of chemical elements in peatlands. The few publications which are available focused mainly on detrital minerals and the weathering processes of them (Bennett et al., 1991; Steinmann and Shotyk, 1997; Le Roux et al., 2006; López-Buendía et al., 2007; Rydelek, 2011). Furthermore, framboidal pyrite and biogenic silica are commonly described in addition to micrometeorites, which occur only rarely in peatlands (Franzen, 2006). As a result, the peatland mineralogy seems to be very simply and unimportant from the point of view of PTE mobility.

On the other hand, it is known that soils in and around industrial centres or large urban agglomerations are significantly enriched in trace elements due to atmospheric deposition

(e.g. Lis, Pasiieczna, 1995). Dust particles contribute significantly to PTE deposition and dominate over PTE deposited in dissolved form close to the industrial centres (np. Batonneau et al., 2004; Raush et al., 2005). The phase composition of dust pollutants emitted by industry is very complex and differentiated, often specific for a given emission source. The anthropogenic particles vary distinctly from the natural particles (minerals) in relation to their structure, morphology and chemical composition (Querol et al., 1996; Jabłońska, 2003; Magiera et al., 2011).

The aim of the conducted investigations was to get the basic knowledge of the complexity of mineral components in peatlands polluted by atmospheric deposition and to identify particles hosting PTE in peat. Furthermore, I aimed to determine the reactivity of anthropogenic particles in peatland environments, to recognize the processes of dissolution and precipitation of mineral constituents and to recognize the influence of these processes on the mobility of PTE in peatlands. Another important aim was to fill a clear gap in the knowledge on the role of mineral constituents (both anthropogenic and natural particles) on peatland biogeochemistry. The presented scientific achievement is the first comprehensive and detailed contribution to the knowledge about PTE mobility, which takes into account mineralogical composition of the polluted peatlands.

The presented scientific achievement is based on investigations conducted in the years 2009-2012 during the realization of research project “*The influence of biogeochemical processes on the cycling of trace elements in peatlands polluted by dust deposition*” (N N304 319136) granted by MNiSW, in which I was the principal investigator. The research was carried out in poor fens located in a forest complex on the northern limit of the industrial part of Upper Silesia. A small, partially natural mire located in an eastern part of Upper Silesia conurbation and exposed to a long-time deposition of high amounts of pollutants was the subject of studies carried out during a three month stay in a Geobiology Centre in University of Bergen. The study was realized during a research project “*The influence of biogeochemical processes on the cycling of toxic elements in the environment*” (FSS/2008/V/D3/W/0012) financed by Scholarship and Training Fund. A piedmont ombrotrophic peatland located in the Orawa-Nowy Targ Basin, was studied as an example of peatland with low deposition of pollutants originated from distant sources. Since 2011, in collaboration with the Institute of Biogeography and Paleoecology of the A. Mickiewicz University in Poznań, we have been conducting a multidisciplinary investigations on the pollution of Sudety peatlands within research grant “*Multi-proxy study of atmospheric pollution and paleoenvironmental change in two mountainous peatlands in south-western Poland*”. I have been contributed as a co-investigator in the research grant financed by NCN. The first results, indicating a change in microorganisms composition due to extremely high dust deposition to the peatland located in Izery Mountains, are also included in the scientific achievement. The common feature of the investigated peatlands is the origin of pollutants which are received from atmospheric deposition in both dissolved and solid state.

In the presented scientific achievement, I documented the occurrence of numerous inorganic particles which are characterized by high diversity of chemical composition, morphology and dimensions no larger than the tens parts of a millimetre. I confirmed, that mineral components are the hosts of many PTE, e.g. Zn, Cd, Ba, Mn, Ni, Cu, Pb, Sn, Sb, W and probably Tl and As. PTE occur in the particles deposited from the atmosphere and also constitute the main component of minerals, which formed in the peat as a result of biogeochemical processes occurring in the studied peatlands.

Because of the general lack of studies dealing with the mineralogy of peatlands polluted by PTE, my own studies I initiated by proposing a classification and division criteria of mineral components occurring in peatlands. I used scanning electron microscopy (SEM) as a main method of the investigations. In the publication [1], I proposed a classification which took into account the origin of mineral components. I divided into two main groups the particles observed in peat: dust particles of both natural and anthropogenic origin and minerals formed in the peat. The grouping was done mainly by conducting microanalyses of the particles using EDS (Energy-dispersive X-ray spectroscopy) and by analysing their morphology. The spatial relation to organic debris was often the most important feature enabling the recognition of authigenic minerals. I often observed mineral components which had the same or similar chemical composition but differ in the origin. For example, both dust deposited zinc sulfides and ZnS directly formed in peat due to microbiological processes occurring in the peatlands located close to the Upper Silesia conurbation (publications [1], [2], [3], and [6]).

In publication [2] I presented a method invented to obtain a quantitative information about the amount of particles in a peat. The method involves counting of particles within grid test points in uniform increments, adjusted to the size of particles which are to be analysed. By using the EDS detector it was possible to get the information about chemical composition of mineral components counted in the consecutive grid points. The SEM point-counting method enables to document variations in the amount of particles in vertical peat profiles and also enable to quantify differences in particles number between peatlands located at different distances from emission sources. The sample homogenization process, necessary to conduct the analyses and obtain repeatable results, cause a loss of part of the information, especially that related to the origin of some of the particles. The SEM investigation revealed that the inorganic particles in the investigated peat cores fall into five groups based on elemental composition and morphology, namely, feldspars, spheroidal aluminosilicate particles (SAP), nondescript aluminosilicate particles (mainly clay minerals and aluminosilicates for which more detailed identification was not possible), silica (quartz and biogenic silica) and Fe (hydro)oxides in the peatland located in Orawa-Nowy Targ Basin. The number of groups results from the possibility to identify all the particles present, often very small ($\geq 1\mu\text{m}$) and the amount and type of particles occurring in peat. Based on the results obtained for other peatlands (e.g. Siberian peatlands), it seems that the grouping reflects the basic diversity of mineral components in peatlands, regardless of the amount of deposited dust and level of contamination. Additionally, barite (up to 0.6%) and ZnS (up to 1.1%) were shown to constitute site-specific fractions in the Upper Silesian mires. The method is recommended for

application with peats having ash contents $> \sim 4\%$. Most of the PTE-hosting particles were present in amounts too low to be quantified ($< 0.05\%$) and were deemed accessory minerals/phases. The distinction is important because by analysing peat or other environmental samples using BSE (back-scattered electron) detector it is easy to overestimate the number of particles containing PTE as they appear lighter in comparison to other particles, e.g. aluminosilicates.

At the moment, the SEM point-counting method is the only one that allows to quantitatively determine the amount of inorganic components in peat which differ in chemical composition with defined precision and detection limit defined by the method assumptions. X-ray diffraction method (XRD) can be used as an alternative. However, in the case of ombrotrophic and transitional peatlands the method can be performed only after removal of the dominating organic matter. The removal procedure might transform or destroy some of the mineral components. XRD studies also fail to detect noncrystalline inorganic components and, thus, predominantly glassy inorganic fly-ash particles and tephra shards remain undetected or under-represented.

Using the SEM point-counting method I showed in publication [2] that the upper peat layers contain a variety of different particles which amount decrease below a certain depth range, which is a characteristic feature of every peatland. The lower amount and reduced differentiation of mineral components in deeper peat layers results from the overlapping of two processes. Changes in atmospheric pollution result in changes in the amount and type of inorganic particles deposited on the peatland surface. Both the number and variability of particles were lower in the preindustrial times. Because the inorganic particles show variable resistance to the conditions prevailing in a peat, important part of the particles undergo dissolution, and the rate of the particles decomposition depend on both the type of particle and the conditions specific to a particular peatland ([1] and [2]).

Another important criterion, which I have distinguished while analysing the mineral components occurring in peatlands, is the stability of the inorganic particles against peat environment. Especially important is the stability of anthropogenic particles. This problem has been most fully characterized in a publication [1]. I have taken into account the degree of dissolution of individual particles, the changes in the number of particles which proceed down the vertical profiles and the history of industry development in the region, while determining the stability of anthropogenic particles. I have compared the mineral components observed in the peat profiles with phase composition of dust particles deposited on green parts of plants growing on the peatland. The particles in peat were also compared with the results of long-time studies of mineral composition of atmospheric dust in Upper Silesia conurbation. The peat profile was dated and the age of peat and accumulation rate of each peat layer determined using ^{210}Pb method. The polluted peat layer was determined by analysing selected metal concentrations and ash content. The peat contained increased concentrations of Zn, Pb, Cd and Cu within the depth range of 0-28 cm.

The iron (hydro)oxides, commonly enriched in Zn and rarely in Mn, Mg and Sn I have classified to particles unstable in the peat environment. They are abundant in the uppermost peat layer (0-8 cm) and almost absent below this depth range. Also the ZnS and PbS particles

are slowly dissolving in the peat, similarly to the rarely occurring Pb chlorides and complex metal oxides. Fe sulfide was found to be unstable in ombrotrophic and transitional peatlands. The mineral was absent in the peat while occurring on the peat surface. Conversely, I have observed very porous due to dissolution PbS grains up to the depth of 32 cm. This indicates that the relicts of galena can survive even 150 years, provided that their displacement down the profile is limited. The dissolution of both the oxides as well as sulfides is obtained due to the specific conditions of the peat accumulating environment where two layers can be distinguished, an upper, oxygen-rich, more acidic acrotelm and a lower, more reducing catotelm. Each inorganic particle is first subject to the more aerobic conditions of the acrotelm, before being buried deeper in the mire as the peat accumulates. By measuring the water table level during an almost two years period, I was able to demonstrate that significant seasonal fluctuations of water level (up to 50 cm) occur in the peatland. The fluctuation had a great impact on redox conditions on an annual scale and promoted the release of metals from dust particles. Especially that in peatlands which get dry because of extensive drainage, the entire metal polluted layer stays periodically above the water table level [1].

In a next publication [4] I have confirmed the influence of anthropogenic dust particles on the chemistry of pore water in the studied peatlands. I have conducted physico-chemical analyses of pore water collected at two depth ranges and during different seasons. The measurements allowed me to confirm that the instability of anthropogenic particles has a significant impact on the concentrations of some PTE in pore water. I have compared the metals concentrations in pore water, precipitation and metals content in peat and have shown that the metals stored in peat do not influence the chemical composition of pore water as long as the water table position is high. However, two groups of elements have been distinguished. I have shown that the concentrations of Pb, Cu, Tl, Cd and Zn in pore water are comparable to mean annual concentrations in precipitation in the region during the study period. During the same time, the concentrations of Fe, Mn, As and Ba are several times higher in pore-water than in precipitation. This observation was explained by decomposition of metal-hosting dust particles after their deposition on the peatlands. The dissolution of different iron oxides and hydroxides, which are an abundant component of atmospheric dust, is responsible for the increase in Fe, Mn, Zn and As. I have also found out that the one order of magnitude higher concentration of Ba in pore-water than in precipitation resulted from the dissolution of barite - a common dust component in the Upper Silesia region. I have confirmed the instability of barite in the peatland environment using SEM. I have proposed that barite dissolution is achieved by both the reducing conditions and elevated concentrations of dissolved organic matter (DOM), which I documented for the peatlands [4]. This explains that barite was lacking in the waterlogged peatland, but have been confirmed to precipitate in the peatland characterized by high variations in water table level [2]. Zinc, released from the iron (hydro)oxides, precipitate as zinc sulfides in the peat, keeping the concentrations of Zn in pore water similar to concentrations in precipitation [1].

The pore water measurements conducted during an almost two years long period and described in publication [4], let me to observe high variations in PTE concentrations in peatland pore water. Increase of PTE in pore water correlated with decrease of pH value and

rewetting after dry seasons characterized by low water table position. At the same time, little variation was observed in a peatland, in which constantly-high water-table was maintained. I have shown that the lowering of water level results in rapid release of PTE accumulated in peat to pore water. The PTE release occur periodically, most commonly during autumn season. For one of the studied peatland, I documented an almost 13-fold increase of Cd and Tl concentrations, 6-fold increase of Mn, Zn, and Ba concentration and around two-fold increase in Pb, Fe and Al concentrations in relation to average values from the waterlogged season. Moreover, I have shown that high variations of water level lead to constantly high concentrations of Pb, Zn, Ba, and Al.

Unfortunately, with the majority of peatlands being drained in Europe, peatland drying and high variations in water position are common for most peatlands. The fully waterlogged state is unusual and, if no maintenance is applied, require same unique meteorological conditions to occur. In the case of my own investigation, the high water level was obtained due to severe central-European flood event in 2010. Long-time studies of natural peatlands conducted in Białowieża National Park indicate a slow lowering of water table in peatlands as a consequence of climate changes (Czerepko, 2011). My own studies show the danger of pulse releases of stored trace elements as a consequence of peat dryness and confirms the need for suitable water management in peatlands with regard to the cycling of potentially toxic elements and the necessity to protect water-logged biotopes.

Among the mineral components of atmospheric dust, some are characteristic to a defined source of emission (e.g., coal combustion, non-ferrous metal smelting, transport). They constitute the mineral tracers of pollution sources (Jabłońska, 2013). By identifying them in peat, I was able to show the spatial and temporal range of pollutants dissemination from a known emission source. My research shows (publications [1], [2] and [5]) that all the peatlands located in southern Poland contain spheroidal aluminosilicate particles (SAP). The observed particles were often hollow or porous and originated from the deposition of dust emitted by coal-fired power stations. While it is thought that they are carriers of many PTE, especially the volatile elements, which condense on their surface, their basic composition is simple. They are aluminosilicates of Na, K, Mg, often with traces of Ca and Fe. Ti constitute a common admixture, often up to a few weight percent. In contrast to spheroidal Fe oxides, which are also unambiguously technogenic in origin, SAP are stable in the peaty environment. Therefore they are perfect tracers of industrial origin of dust in peat profiles. They can be especially useful to determine the beginning of industry influence on changes of metal content in peat vertical profiles. In most cases, the determination of metals mobility or immobility is the most demanding task while interpreting the paleo-environmental changes using peat.

I have shown in publication [2] that the beginning, the maximum and a decrease in the number of SAP in the youngest layers can be determined in each peatland. I showed also that they are very common constituent in the peatlands. In the peatland located in the Orawa-Nowy Targ Basin SAP constitute 17% of all analysed particles at maximum concentration. They constitute 39% of all inorganic particles, dominating over SiO₂, in peatlands located close to the Upper Silesia region. In Izera Mountains, the maximum concentration was 66% of all particles present in peat polluted by dust deposition originated from lignite combustion

in power stations [5]. The pronounced reduction in dust emission recently is seen in the decrease of the amount of SAP in the uppermost peat layers, which contain between 0 and 5% of SAP ([2] and [5]).

By analysing the dimensions of SAP, I have shown in publication [2] that the distance from fly-ash emission source is the main factor determining their size. The peatland in Orawa-Nowy Targ Basin, located far from industry centres, hosts the smallest SAP. The average SAP size in the Upper Silesia peatlands was distinctly larger. Interestingly, the introduction of particle control systems in power stations is not reflected in profile grain size distributions. The generally uniform SAP size with depth seems to confirm that distance is the main size-controlling factor.

I have analysed a mineral composition of an ombrotrophic peat bog located in Izery Mountains, within the borders of Nature Reserve “The Peat Bogs of Izera Valley”. At the same time the peat bog is located in an area called the Black Triangle, which is the most polluted region in Central Europe. Changes in the community structure, functional diversity, and mechanisms of shell construction in testate amoebae were documented as a result of an extreme atmospheric pollution during the last 50 years. In publication [5], with collaboration with Joint Institute for Nuclear Research in Dubna, and the use of epithermal neutron activation analysis (ENAA), a relatively low concentrations of PTE (e.g., Cu, Ni and Cr) were documented in contrast to extremely high concentrations of Al and Ti in peat. By using SEM imaging and the invented SEM point-counting method, I have been able to document a very common occurrence of large (>50 µm), porous particles with high Al content ($\text{Al}_2\text{O}_3 > \text{SiO}_2$) and SAP of an average size 2.6 µm in the peat samples. I have made a very interesting observation while analysing the mineral composition of shells build by testate amoebae of *Diffugia sp.* and *Phryganella sp.* SAP constituted the basic component of shells of this microorganisms. Conversely, the decline of silica-biomineralizing testate amoebae is probably related with the toxic influence of aluminium. The high content of Al in the deposited dust together with the low pH of the peat bog lead to the leaching of the toxic element to peat pore water.

The analysis of the amount and chemical composition of SAP in peat lead to a conclusion, that titanium, which is commonly considered as conservative, lithogenic element, used as a proxy for soil-dust contributions to trace-element concentrations in peat, is also of anthropogenic origin in the upper peat layers. Ti enrichment up to few weight percent is typical of the SAP composition, therefore cannot proxy for soil dust in peat ([2]).

The disclosure of the mechanisms of biogenic sulfides formation in peatlands was one of the most important achievements of my investigations. There is a general lack of mineralogical investigations directly proving *in situ* precipitation of sulfide minerals and their importance in metal containment in peatlands. The mineral content, the rate of their formation as well as the size, shape, chemical compositions and distribution in organic matrix were poorly known. The presented research is one of the first showing that the pollutants deposited from the atmosphere can be immobilized in authigenic metal sulfides. Certainly, for the first

time, the conducted research fully describes the process of authigenic metal sulfides formation from both the mineralogical and biogeochemical sites.

The first observations of authigenic zinc sulfides are described in publication [1]. The investigations were continued to determine mechanisms of metal sulfide formation and to define the conditions most favourable for their precipitation and stability in peatlands. Therefore, I have conducted geochemical modelling based on seasonal measurements of physico-chemical parameters of pore water. The results are described in publications [3] and [6]. The observations that confirmed the participation of microorganisms in Zn, Pb and Cd sulfides precipitation were conducted during a three-month stay in Geobiology Centre of the University of Bergen by using a high-resolution SEM, designed for the investigations of mineral-microorganisms interactions ([6]).

Zinc sulfide, often with the addition of Cd (up to ~4 wt%), was the most commonly observed biogenic mineral. The mineral occurred only in peatlands suffering from the pollution emitted within the Upper Silesia industrial region. In the transitional peatlands located north from the industrial region, zinc sulfide was the main sulfide which precipitates in the peat. Moreover, I confirm the presence of small inclusions of authigenic galena in the peatlands, while iron sulfides were lacking despite the dominance of Fe over Zn in both the peat and pore water. A comprehensive discussion on the issue is included in [1]. By using a high-resolution SEM with field emission gun (FESEM) I have shown that the zinc sulfides are distributed heterogeneously in the peat, inside tissues of the decayed plant matter, in the form of loose aggregates composed of tens to hundreds of spheroids, 0.3 to 3 μm in diameter. I have also observed hemispheroidal particles, indicating growth after attachment to an organic surface. Some spheroids were empty inside. Moreover, the zinc sulfides were covered and attached to the organic surfaces by microbial biofilm. An interesting observation was that the biogenic zinc sulfides were never found inside *Sphagnum* tissues in spite of the very porous surface of the sphagnum moss and the fact that the moss is the main component of peat. While interpreting the observations, I proposed mechanisms and processes, which explain the zinc sulfide formation in peat [6]. The peat colonization by sulfate-reducing microorganisms (SRM) is heterogeneous in the peat and depends on the resistance of plant debris to microbiological degradation. For instance, the sphagnum litter contains several antimicrobial compounds preventing the moss from biodegradation (Hajek et al., 2011). The inhomogeneous microbial colonization leads to the formation of steep concentration and redox gradients between the inside and outside of plant tissues. The localization inside plant debris as well as coverage by the biofilm prevent the sulfides from oxidation during low water table level and mechanical displacement. The dimensions of the ZnS spheroids depend most probably on the stability of redox conditions, the ZnS spheroids were distinctly smaller in a mire with very thin peat layer [6].

I have shown in publication [6] that even a very thin peat layer (around 30 cm) is sufficient to immobilize PTE in biogenic metal sulfides. Two years-long measurements of physico-chemical parameters of peat pore water, conducted during summer and early spring periods, have indicated predominantly oxidative conditions in the investigated wetland. The observations are important, as it is generally believed and used while constructing artificial

wetlands for water purification, that metal sulfide precipitation require exclusively anoxic conditions. It is also believed that even the oxygenated microenvironments formed along plant roots are detrimental for metal sulfide precipitation (np. Dvorak et al., 1992; Johnson and Hallberg, 2005). I have proposed that SRM plays the key role in sulfide precipitation by lowering redox potential at the microsites and by sustaining disequilibrium conditions between main redox pairs in the wetland pore water. In such conditions, the following sulfides precipitate in decreasing concentrations: pyrite, mainly in the form of framboids, galena, unspecified polymorphs of ZnS, (Cd,Zn)S, and, most likely, barite. According to the knowledge of the author, it is a first description of biogenic galena precipitating in low-temperature near-surface environment. In contrast to the constantly spherical Zn and Cd-Zn sulfides, galena precipitates are very variable in respect of their morphology. I have observed perfect cubes of galena no larger than 0.1-0.3 μm , as well as less regular aggregates of nanometre particles having cuboidal or octahedral outline. Relatively large (up to 2.6 μm) spherical aggregates of PbS occur inside fungal hypha or form encrustation of fungi spores. This indicates enzymatic mechanisms of the minerals precipitation, probably taking place in oxidative conditions.

The correlations of the PTE concentrations have been conducted in the wetland [6]. I have shown a strong positive correlation between Zn, Tl and Cd, suggesting that Tl co-precipitated with Zn and Cd in sulfides. Lead concentrations correlated positively with Cu and As. The Pb and Cu co-occurrence in galena I have confirmed by the EDS microanalysis.

The occurrence of barite and unspecified polymorphs of ZnS and galena within the spaces left after the dissolution of crystals of calcium oxalate monohydrate (whewellite) was an interesting finding, reported for the first time in the scientific literature [3]. I have observed the pseudomorphs using SEM imaging in one of the peatlands located on the northern perimeter of the Upper Silesia industrial region within peat layer contaminated by PTE. The replaced calcium oxalate crystals originated from bark of Scots pine living primarily on the peatland. The observation of perfect pseudomorphs of ZnS, barite and inclusions of galena after whewellite and hollow pseudomorphs, partially occupied by the secondary minerals, lead me to propose a sequence of processes which result in the pseudomorphs formation. I have conducted geochemical calculations showing the changes of a saturation index in relation to the values of pH and Eh, and the concentrations of sulfur forms (SO_4^{2-} , S^{2-}), Ba and Zn ions measured in peatland pore water. I have shown that a range of redox conditions exist in which both barite and ZnS polymorphs are stable. The finding is important as both minerals are redox sensitive. Zinc sulfide precipitates under reducing conditions, whereas barite precipitation requires more oxidizing conditions. The Eh range in which both minerals are stable widens with increasing pH. Because the pH of the peatland is low (3.5-3.8), I have proposed that the degradation of calcium oxalate by oxalotrophic bacteria might increase the pH and promote the precipitation of barite and ZnS in the voids, with perfectly preserved shape of whewellite crystals.

Summarizing, the presented scientific achievement comprises a detailed characteristic of biogeochemical processes occurring in peatlands polluted by long-time lasting atmospheric deposition. The role of mineral components, mainly anthropogenic particles and biogenic minerals, in the cycling of elements which are potentially toxic to the environment was the main subject of the investigations. As most of the investigated peatlands were located close to the Upper Silesia conurbation, I investigated in details the biogeochemistry and mineralogy of lead, cadmium, zinc and barium, and also arsenic, thallium and copper. I conducted the mineralogical investigations using scanning electron microscopy and x-ray diffraction to a lesser extent. I have also analysed total concentrations of selected elements in peat profiles. Main part of the investigations comprises physicochemical analyses of pore water conducted seasonally.

To the most essential scientific achievements I include the demonstration that mineralogy is important in biogeochemical investigations of peatlands, because mineral components, if present in the peat, affect PTE cycling. I have proposed the classification and division criteria of mineral components in polluted peatlands taking into account their origin, stability and PTE content.

An important achievement was the indication of amorphous spheroidal aluminosilicate particles (SAP), originated from coal combustion, as a mineral tracer of industrial pollutants. I have shown that SAP are an important component of peat, dominating over geogenic dust particles in some of the investigated peatlands. In view of the characteristic shape and the confirmed by investigations stability in peat, SAP can serve to determine the spatial and temporal range of human influence on atmospheric dust composition in peat profiles. An interesting manifestation of the common occurrence of SAP in peat was their adaptation to shell construction by testate amoebae.

The next important achievement was the documentation of the immobilization of atmospheric pollutants in metal sulfides due to biogeochemical processes occurring in peatlands. Zinc sulfide with an admixture of Cd was the most common biogenic mineral in the investigated peatlands, occurring inside partially decayed plant matter. In one of the peatlands I have discovered biogenic galena of diversified morphology. Based on the investigation of an initial peatland characterized by thin peat layer, I have shown that the precipitation of metal sulfides do not require exclusively anoxic conditions and the lack of thermodynamical equilibrium between different redox couples favour the formation of sulfide minerals. The complexity of processes occurring at the micro-scale in the environment I have shown using as an example the formation of pseudomorphs of zinc sulfide and barite after whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), in a bark of a scots pine preserved in the peat.

5. The description of other scientific achievements

a) The description of scientific achievements obtained before PhD degree

During my master studies I started to investigate fossil organic matter containing high concentrations of uranium. In 1999 I defended my master thesis: *Oxyreactive Thermal Analysis (OTA) of Proterozoic organic matter from the natural nuclear fission reactors in Gabon*. In the study I used very unique samples from an uranium deposit Oklo-Okelobondo in Gabon (west Africa), where self-sustaining nuclear chain reactions have occurred in uraninite aggregates approximately 2 billion years ago. Part of the study material I collected personally in a repository of drill cores of the Natural Nuclear Fission Reactors at the Surface Geochemistry Centre, CNRS, in Strasbourg, France. The research aimed at evaluating the applicability of oxyreactive thermal analysis (OTA), developed at the beginning of 90th (Cebulak and Langier-Kuzniarowa, 1997), to investigate strongly mineralised and thermally altered organic matter. I confirmed the hypothesis that the OTA analysis allows to differentiate between different types of organic matter. The organic matter structure, genetic differences and the degree of transformations can be determined using OTA.

I have continued the investigations of uraniferous organic matter during my PhD studies. I used an uraniferous organic matter (1.2-15 wt% U) from the Proterozoic uranium-gold deposit in Witwatersrand, South Africa, in addition to the material from Oklo-Okelobondo. The main aim of the research was to determine the degree and type of transformations occurring in the structure and chemical composition of the organic matter caused by a long-term radiation emitted by radioactive minerals. The uraniferous organic matter formed an exceptional experimental design with an exposure time of over two billion years. I aimed to obtain a better understanding of the applicability of bitumens to immobilize radioactive wastes.

A new and interdisciplinary methodological approach was invented to study the uraniferous material. Some of the methods were used for the first time in studies of uraniferous organic matter, including the OTA method. A research grant (KBN 2 PO4D 012 26) *The application of Oxyreactive Thermal Analysis (OTA) in the study of uraniferous organic matter* obtained in 2004, allow me to include into the methodology high-resolution transmission electron microscopy (HRTEM). The organic matter was observed using a *lattice fringe* technique at Centre de Recherche sur la Matière Divisée, CRNS in Orleans, France (11-12.2004), in cooperation with J.-N. Rouzaud, a specialist of carbon materials. By adding optical microscopy and X-ray diffraction analysis (XRD), I was able to fully characterize the structure and texture of the organic part of the samples. The uranium mineralization was analysed using SEM and XRD after removal of the organic component of the samples.

In the PhD theses defended in 2005, entitled *The application of Oxyreactive Thermal Analysis (OTA) in the studies of uraniferous organic matter* I have confirmed that ionizing radiation cause dehydrogenation and a relative increase of aromatic rings (planes) in the structure of organic matter. The increase of structure aromaticity advancing from the radioactive mineral cause the formation of radiation halo. The radiation halo in immature organic matter was characterized by elevated reflectivity values. An early dehydrogenation decreased the susceptibility of organic matter close the uranium minerals to structure reorganization by pressure increase and temperature. I demonstrated for the first time that mineralized bitumens can show a complex and differentiated optical symmetry resulted from

the influence of both the ionizing radiation and tectonic stress different than lithostatic pressure.

I demonstrated that ionizing radiation emitted by radioactive minerals does not induce oxidation of organic matter, as previously thought (e.g., Hofmann,1993). Some part of the organic matter associated with natural fission reactors is oxidized due to the influence of oxidizing solutions originated from water radiolysis resulted from the fission reactions. The coexistence of the primary and oxidized organic matter allow to explain differences in chemical composition and structure of organic matter associated with the natural nuclear fission reactors.

I have proven that ionizing radiation has no influence on the size of polyaromatic planes and the degree of ordering of the organic matter structure. Therefore, based on the obtained results, the modification of organic structure resulted from the ionizing radiation are not comparable to the changes resulted from coalification. The light halo effect around uranium-hosted minerals disappears with increase of degree of coalification. The rigid structure of organic matter from the radiation halo in highly coalified organic matter has the same or comparable reflectivity values and its optical anisotropy is lower than the surrounding organic matter. In the highly coalified organic matter in Witwatersrand deposit, radiation halo is distinctly visible because of different optical symmetry in relation to the bulk organic matter.

The results of the investigations I presented at subsequent meetings of the Polish Mineralogical Association in Poznań (2001), Cieszyn (2003), and Krościenko (2005). I presented the results of OTA analyses during „8th European Symposium on Thermal Analysis and Calorimetry” in Barcelona in 2002. The results from OTA analyses were published in a journal indexed in Journal Citation Reports (*Smieja-Król B. (2003) Analysis of organic matter from Witwatersrand basin (South Africa) by OTA and Py-GC-MS. Preliminary results. Journal of Thermal Analysis and Calorimetry 72, 383-391*). The results indicating the complex structure and optical symmetry of organic matter from Witwatersrand deposit were published in International Journal of Coal Geology (*Smieja-Król B., Duber S., Rouzaud J-N. (2009). Multiscale organisation of organic matter associated with gold and uranium minerals in the Witwatersrand basin, South Africa. Int J Coal Geol 78, 77-88*). In 2006 I get prime Minister's Award for Outstanding Doctoral Dissertation (Warszawa, 15.12.2006).

At the same time, together with S. Cebulak I conducted investigations on the applicability of OTA in the studies of fossil organic matter. The possibilities of the usage of the method to characterize the properties of different carbon materials were presented in the publication: „*Cebulak S., Smieja-Król B., Duber S., Misz M., Morawski A.W. (2004) Oxyreactive thermal analysis a good tool for the investigation of carbon materials. Journal of Thermal Analysis and Calorimetry 77, 201-206*”. The results of a research on self-ignition of coal wastes were presented at the conference of Polish Geological Association in Rybnik in 2005.

b) The description of scientific achievements obtained after PhD defence

After the defence of doctoral dissertation I continue for a few years the investigations of fossil organic matter using OTA as the main method. I was a co-investigator in a research grant entitled: *Transformations of organic matter in the rocks deposited in coal waste dumps* (N307 016 32/0493 MNiSW), realized in the years 2007-2009. The obtained results of thermal properties and the susceptibility of coals from the Upper Silesia Coal Basin to self-ignition were presented at the First Geological Congress in Kraków in 2008 (Attachment 4, II. H10 and II. H11). Results of master thesis realized under my protection were presented at the International Committee for Coal and Organic Petrology (ICCP) meeting in Belgrade in 2010 (Att.4, II. H12). The study focused on transformations occurring in coal wastes while thermally treated in oxygen free atmosphere. Thermal characteristics of coals of Łaziskie Beds from the Jaworzno coal mine was included in publication in *Zeszyty Naukowe Politechniki Śląskiej* (Att.4, II.B1).

In the meantime, my research interests turn into biochemistry and environmental mineralogy. The milestone event was, in addition to the research stay in Bergen, my attendance in a course on *Environmental Chemistry of Heavy Metals* in Heidelberg (theoretical part) and Harz Mountains (practical part), organized by W. Shotyk and M. Krachler in 2009. J. Nriagu, one of the greatest authorities in environmental geochemistry was a co-host of the course. In the field of environmental geochemistry and mineralogy, I am most interested in the seasonal variability and the dynamic of processes occurring at the Earth surface. I found also interesting the ephemeral state of biominerals which undergo everlasting transformations providing information about the ongoing near- surface processes. An expression of the interest is the research on the biogeochemistry and mineralogy of polluted peatlands, which I devoted the most time and commitment. As I am interested in the dislocation of PTE indifferent compartment of the biosphere, I have participated in investigations conducted by different research teams.

Similar to the topic of my scientific achievement are extensive, interdisciplinary investigations of ombrotrophic peatlands of southern Poland and Siberia conducted in cooperation with the researchers from the A. Mickiewicz University in Poznań, Technical University in Gliwice, Institute of Nuclear Physics PAN in Kraków and Joint Institute for Nuclear Research in Dubna. Within frames of the research, the analysis of peatlands from the northern limits of Upper Silesia industrial region was conducted to elucidate their effectiveness in carbon sequestration (Att.4, II. A5). On the basis of ^{210}Pb and radiocarbon (AMS) ^{14}C dates and age-modelling, 7000 and 2000 year high-resolution records of paleoenvironmental changes and changes in carbon accumulation rate (CAR) were presented. In addition to changes induced by human activities, for instance drainage, the influence of climatic changes on carbon accumulation rate was visible. The increase in CAR values were noted during 'Medieval Climatic Anomaly' in the peatland less affected by human activities. Minor climatic signals linked to the 'Little Ice Age' and to the influence of wind-blown sands were also evidenced. Most importantly, we have demonstrated that the peatlands exhibit higher rates of carbon accumulation compared with boreal regions during the last 200 years.

At Mukhrino ombrotrophic peatland, located in Western Siberia, we have analysed the concentration of 36 elements by using the ENAA method, mineral composition and CAR in all the ^{14}C dated peat layers. The results were published in Scientific Reports (Att.4, II. A7). We have distinguished the influence of natural and anthropogenic anomalies on the amount as well as elemental and mineralogical composition of dust deposited on the peatland during the last 8000 years. We have demonstrated that the increase in dust deposition in the lower part of peat profile was related with a long-lasting dryness with a maximum at the turn of XV and XVI century. An abrupt change in the carbon accumulation rate (CAR), the occurrence of mullite and large amounts of micro-charcoal particles was documented for a peat layer of an age of AD 1882 \pm 43 – 1920 \pm 28, indicating the possibility of dust deposition which originated during the Tunguska catastrophic event. I have evidenced the occurrence of spheroidal aluminosilicate particles (SAP) in the peat, which is located as far as possible from any industrial source of emission, what was very important achievement of the investigations. SAP were observed in the upper part of the peat profile starting from a layer dated on 1958. Because SAP are unambiguously technogenic in origin, we propose to use them as markers of a newly proposed epoch – the Anthropocene. The second important achievement of the study was to show that the highest amount of dust was deposited on western Siberia in 1962 as a result of nuclear weapon testing in the atmosphere. The nuclear tests influenced the chemical composition of the dust, which was enriched in rare earth elements and uranium.

Furthermore, studies on the origin of air pollutants are conducted using ombrotrophic peat bogs in Sudety mountains. We are investigating changes in the atmosphere pollution over the centuries based on the analysis of trace elements concentrations and stable lead isotopes. The preliminary results showing the changes of uranium concentrations in the vertical profile of a peat bog from Hala Izerska have been presented at the Society for Environmental Geochemistry and Health (SEGH) conference in Newcastle in 2014 (Att.4, II. H21). The results obtained for Śnieżka peat bog are under elaboration. My own achievement in the interdisciplinary research is the finding of mullite in upper part of peat profiles collected from peatlands and bogs from southern Poland. Mullite is a rather exotic natural mineral. On the other hand, it is emitted in large quantities by coal-based power stations due to high-temperature transformations of clay minerals. As such, it is a perfect marker of technogenic dusts in peat. Because mullite is stable in high temperatures, the XRD analysis can be applied after ashing of peat samples. Preliminary results, showing changes of mullite concentrations in peat profile in peat bog at Hala Izerska were presented at SEGH conference in Newcastle in 2014 (Att.4, II. H20). At maximum, mullite accounts for 43% of crystalline part of ashed sample. The high content of mullite correlates with a significant increase in concentration of Ti, V, Cr, Ni, Cu, Ba, and W together with aluminium observed at 10-13 cm, related to extremely high dust emission from the nearby Turów lignite-based power station in the late 70's of the last century. A publication revealing methodological details and the possibilities to use mullite as an indicator of technogenic dusts is during preparation. The relation of mullite to the already described SAP will be discussed.

The next subject undertaken in my research is the impact of industrial waste deposits on the environment. The investigations are conducted with cooperation with researchers from

the Central Mining Institute in Katowice. The release of pollutants from waste deposits to natural waters during runoff events occurring after heavy rains has been investigated. Mineralogical analyses of the outer layer of the wastes, in particular the analysis of secondary minerals forming on the surface after longer period of dryness, are my part of the investigations. The first research of this kind was done for a flotation waste dump from Zn-Pb exploitation. Due to the carbonate type of the wastes, the analysed waters were alkaline (Att.4, II. A2 and II. A3). We demonstrated a relationship between changes occurring in the mineralogical composition of the outer layer of the dump and the chemical composition of runoff water. The secondary sulphates and chlorides (e.g. Pb chloride), which dominate in the surface layer in comparison to the deeper parts of the dump, determined the chemical composition and pollution state of runoff water (Att.4, II. A2). We demonstrated that Ca ions and sulphates dominate in the runoff and zinc is the main trace element. We observed an inverse correlation between the amount of precipitation in five days preceding the runoff event and the concentrations of most of ions in the runoff. The exception was the bicarbonate ion which showed a positive correlation. This was related with the dissolution of calcite although calcite is not the main component of the wastes. The observed by SEM highly weathered calcite grains were a characteristic feature of the surface layer of wastes in addition to efflorescence of gypsum (Att.4, II. A3). The investigations showed very well the influence of changeable weather conditions on the dynamic of processes occurring on the dump surface where the mineral composition depended on the amount and intensity of precipitation.

We analysed also the behaviour of elements in iron slag dump located near Kraków, southern Poland (Att.4, II. A8). We documented the occurrence of several elements, including trace elements (i.e., Ag, As, Cd, Cr, Mo, Ni, Pb, Rb, Sb, Sn, and Zn), in the slag, in leachates which formed a pond at the base of the dump, and in carbonaceous tufa accumulations. We showed that the slag is rich in Cr, V and Zn. Extremely alkaline leachates contained high sulphate and K concentrations and elevated concentrations of fluoride and Al. A dominant feature of the leachate was massive precipitation of calcareous tufa forming a cascade of tufa barrier-ponds. The tufa preferentially concentrated Pb, Sr, Ba, Rb, sulphur, and phosphorus while Fe, Zn, Mg, Mn, Cr, and V were depleted relative to the concentration in the slag material.

Recently we are investigating the development of extremely acid waters during the surface runoff at a coal waste dump located within Upper Silesia Coal Basin. I am identifying the phases which form yellowish-white efflorescence on the dump surface after longer precipitation-free periods. I am also investigating the changes in the efflorescence composition in relation to the season and weather changes.

An additional outcome of my research interests on PTE displacement between different environmental compartments is a publication (Att.4, II. A6) which compiles investigations done during master thesis preparation of a student of environmental protection. We proved that barium, which is regarded as an immobile element in the environment, bioconcentrates in hard tissues of mammals. We found elevated Ba content (up to 351 ppm) in freshly cast antlers from male roe deer of different ages collected in Balin near Chrzanów and in the vicinity of Żywiec, southern Poland. Elevated concentrations of Ba in antlers most

probably originated from direct uptake of airborne barite nanocrystals through the respiratory system and/or by digestion of barite-rich dust particles deposited on plants. Burning of Ba-enriched coals is regarded as the principal source of Ba in the investigated areas inhabited by roe deer. Increased concentrations of Ba in antlers from the Żywiec area compared to Balin reflect particularly high air pollution caused by coal-burning mostly for domestic purposes combined with an unfavourable topography that impedes efficient air circulation.

My scientific achievements are presented also in publications reporting the discovery of new springs with active calcareous tufa precipitation. Hard water spring habitats with the communities of *Cratoneurion commutati* belong to priority habitat types designated by European Union as particularly deserving intensive conservation care (Council Directive 92/43/EEC). As a consequence, there is a need to recognize their location, state of preservation, differentiation, the dynamic and the direction of changes and to identify threats and define the needs for conservation management. During a field work carried out over floral composition in spring areas in the Tatra National Park, together with PhD student from the Szafer Institute in Kraków, we documented for the first time the occurrence of springs with active calcareous tufa precipitation in Tatra Mountains (Att.4, II. B3). Altogether eight calcifying springs were documented among 340 analysed. The calcifying springs were found in Kopieniec slope of Olczyska Valley, in Kościeliska Valley and lower parts of Lejowa Valley. We demonstrated that an important factor facilitating tufa precipitation is the presence of a dense cover of mosses. The high concentration of Ca and HCO₃ was not the determining factor as in comparison with typical tufa depositing springs, the values appeared to be rather low. The dense carpet of bryophyte slows down the water flow, serves as a nucleation site for the carbonates, take up CO₂, increase water evaporation. This induces supersaturation of water in relation to calcite at a short distance from the water outflow leading to tufa precipitation at the spring. By continuing the field work in other parts of the Polish part of Carpathian Mountains, we described tufa precipitating springs in Jamne Valley (Att.4, .II. B6) located in Gorce Mountains. I documented the changes in pH, electrical conductivity and concentrations of Ca and Mg ions occurring in spring water due to calcite precipitation.

The investigations of calcifying springs are continued. At present, the results of field and laboratory studies leading to a complex description of springs with active calcareous tufa precipitation in Pieniny National Park are elaborated.

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