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MINERAL COMPOSITION IN RHIZOSPHERE OF PLANTS GROWN IN THE VICINITY OF A ZN-PB ORE FLOTATION TAILINGS POND. PRELIMINARY STUDY

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Mineral forms in rhizosphere and bulk substrate were examined for selected plant species (*Cardaminopsis arenosa, Calamagrostis epigeios, Deschampsia caespitosa, Festuca ovina, Silene vulgaris, Viola tricolor*) growing spontaneously in the close vicinity of a tailings pond and in a zone of eolian transmission of waste particles. Samples of substrates and plant roots were taken from sites in the Bolesław orefield near Olkusz. The substrates together with plant roots were studied by scanning electron microscopy coupled with energy dispersive spectroscopy. Apart from quartz and carbonates, the most frequent mineral phases found were crystalline and amorphous Fe oxides, as well as primary Fe, Zn and Pb sulphides (marcasite, pyrite, sphalerite, galena). Hydrated Ca, Mg and Fe sulphates (gypsum, epsomite and melanterite) and other secondary minerals (smithsonite, cerussite, otavite, and Fe, K and Mg aluminosilicates) were found at larger concentrations in the rhizosphere than in bulk soil, suggesting that plant roots can change the mineral composition of the soil.

Key words: Flotation tailings pond, mineral components, rhizosphere, bulk soil, hyperaccumulator and nonaccumulator plants.

INTRODUCTION

The bedrock hosting major orebodies of Mississippi Valley type (MVT) zinc-lead deposits worldwide is built mainly of carbonates. Apart from the most frequent limestones and dolomites, such lithologies as calcsiltites, shales, claystones and calcareous sandstones composed of quartz, illite and montmorillonite occur within ore units. The type locality is the Mississippi-Missouri area, but MVT Zn-Pb mineralization is found in Belgium (Heijlen et al., 2001), Germany, Ireland (Hitzman and Beaty, 1996), southern France (Leach et al., 2001), near Cracow in Poland (Cabała, 2001) and other places. The mineralogy of the ores is simple; the bulk of economic mineralization consists chiefly of strata-bound lead (galena) and/or zinc (sphalerite) sulphides with associated pyrite and marcasite (FeS_2). Burial of ore-bearing sediments to modest depths followed by unroofing brought primary sulphides near to the surface, where weathering might occur. Components of external layers became dissolved or chemically altered, forming secondary minerals: hydrated Fe, Zn, Pb, Mg and Ca sulphates, Zn and Pb carbonates, and Fe oxides. MVT deposits are a phenomenon of considerable economic value. Zn-Pb ores

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include small quantities of cadmium and silver that are recoverable from concentrates. Elements such as Fe, Mn, Tl, As, Ge, In and Co are present in minor amounts (Żabiński, 1964; Cabała, 1996; Mayer and Sass-Gustkiewicz, 1998).

Wastes from zinc and lead ore mining and processing are commonly stored in huge tailing ponds. This kind of tailings disposal enriches dump surroundings with metal compounds (Górecka et al., 1994). Habitats that develop directly on flotation wastes or in the vicinity of flotation tailings ponds are very hostile environments for living organisms because of the high concentrations of toxic elements (Cd, Zn, Pb, As and Tl). However, many plant species are able to grow in such habitats (Rostański, 1997; Wierzbicka and Rostański, 2002; Dmowski and Badurek, 2002). The roots of these plants can modify their environment and could affect the mineral composition of such habitats.

The rhizosphere is a volume of soil or substrate located close to the root surface, in which physical and chemical properties are changed by root activity. In most substrates the rhizosphere extends from the root surface out into the soil for up to a few millimeters (Campbell and Greaves, 1990). Plant roots are able to modify rhizosphere soil by excretion or reabsorption of H^+ or HCO_3^-, evolution of CO_2 by root respiration, release of O_2, reducing processes, and release of low molecular weight root exudates (e.g., organic acids and amino acids) (Marschner and Römheld, 1996; Gobran et al., 1998).

The pH of the rhizosphere soil may differ from that in the bulk soil by more than two units (Marschner and Römheld, 1996; Gobran et al., 1999 and literature therein). The increase or decrease of pH in the rhizosphere is determined by plant factors, whereas the degree of acidification or alkalization and its extension from the root surface toward the bulk soil are determined by both plant and soil factors (Marschner and Römheld, 1996).

Plant roots can affect the redox potential in the rhizosphere. Under Fe-sufficient conditions, all plants reduce Fe^{3+} chelates and transport the resulting Fe^{2+} into root cells (Curie and Briat, 2003). Under Fe-deficient conditions, most plant species acidify the soil and increase their reduction capacity to reduce Fe^{3+} to Fe^{2+} (Curie and Briat, 2003). On the other hand, during waterlogging some plant species maintain high redox potential in the rhizosphere by O_2 transport from shoots to roots and by release of O_2 into the rhizosphere (Marschner and Römheld, 1996).

Plants release into the rhizosphere many low molecular weight organic compounds such as sugars, organic acids, amino acids and phenolics (Marschner and Römheld, 1996). Among them, organic acids, especially malic acid, and phenolics (reductants) such as caffeic acid, are highly effective in reducing MnO_2, for example, or mobilizing low-soluble inorganic Fe^{3+} compounds in the rhizosphere (Marschner and Römheld, 1996).

Root cap and rhizodermal cells synthesize and secrete mucilage, which consist mainly of polysaccharides and polygalacturonic acid (Marschner and Römheld, 1996). Because surfactants are present in mucilage, the rhizosphere may possess physical characteristics significantly different from those of the bulk soil (Read et al., 1999).

All these processes and released compounds can lead to dissolution of primary minerals and precipitation or crystallization of secondary compounds and/or minerals, and eventually to transformation of mineral components in the rhizosphere. In forest soil, Courchesne and Gobran (1997) observed more intensified weathering of soil minerals in the rhizosphere than in bulk soil.

The present study compared the mineral components of substrate from the rhizosphere of plants and from outside the rhizosphere. The substrate was taken from the vicinity of a Zn-Pb ore flotation tailings pond.

MATERIALS AND METHODS

LOCATION OF STUDY AREA

The study used plant and substrate samples collected in the vicinity of flotation tailings ponds located near Bukowno, Bolesław and Olkusz in the Silesia-Cracow ore district in southern Poland (Fig. 1). Preference was given to sites downwind of the ponds in relation to prevailing southwestern winds (Fig. 1). The sampling locations, labelled A, B and C (Fig. 1), differ with respect to the origin and mineral composition of substrates:

Site A is at the top of the pond. The substrate is made up of Zn-Pb ore flotation waste deposited in 2000–2002. The mineral components of the waste are shown in Figure 2. Humus is absent.

Site B is situated at the foot of the pond, 200–400 m away from the slope. Substrate has formed on quartz sands of fluvioglacial origin. The mineral composition of the substrate is modified by the occurrence of coarse grains of flotation waste rede-

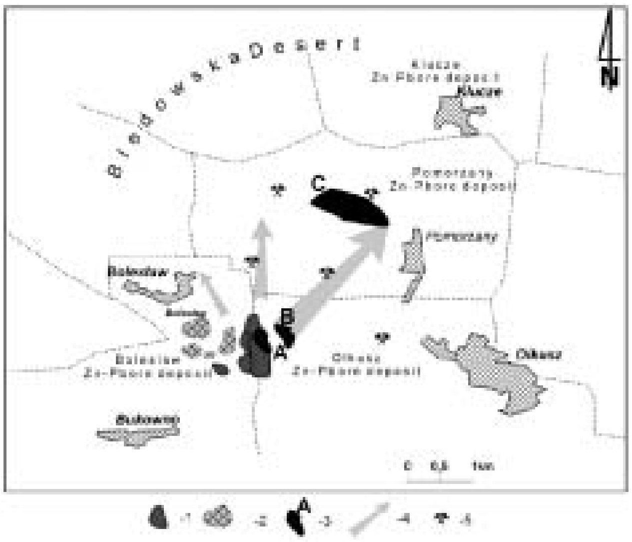


Fig. 1. Sketch map of the examined orefield in the Silesia-Cracow area. 1 – flotation waste ponds; 2 – closed Zn-Pb strip mines; 3 – study area and sample site locations; 4 – dominant directions of eolian transport; 5 – pit shafts.

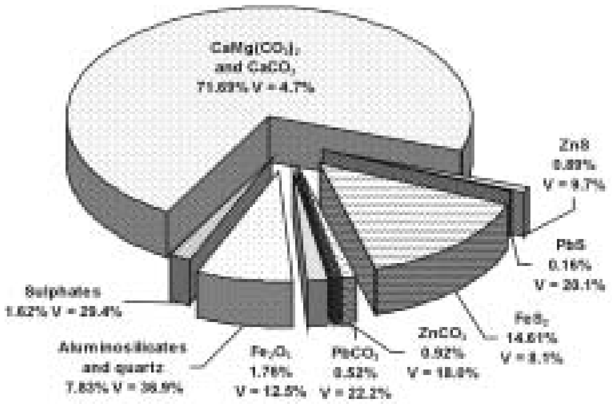


Fig. 2. Mean mineral composition of Zn-Pb ore flotation tailings in the studied area, based on average annual content in 1980-2000. Coefficient of variation V = STD · 100/X (%); STD – standard deviation; X – mean value.

posited by wind or fluid movement. The weakly developed topsoil is 3–8 cm thick.

Site C is located 3 km from the pond. At this site the substrate developed on fluvioglacial quartz sands. The humus layer is not more than 10 cm thick. The rock mass is dewatered, as groundwater is removed by the Pomorzany mine drainage.

TABLE 1. Reaction and electrical conductivity (EC) of substrates from sampling sites; pH was measured in deionized water and in 1 M KCl

Sampling location	pH (H_2O)	pH (KCl)	EC (µS/cm)
A	6.86a	7.37a	640.7a
B	6.83a	7.07a	68.3b
C	5.56b	5.18b	33.9b

Within columns, mean values (n = 3) followed by the same letter do not significantly differ at $p < 0.05$ (LSD test)

SUBSTRATE pH AND ELECTRICAL CONDUCTIVITY

Three substrate samples were collected at each site, air-dried and ground to pass through 2 mm mesh. Substrate pH and electrical conductivity (EC) were measured in deionized water (1:2.5 w:v substrate/solution ratio). Substrate reaction with 1 M KCl was also determined with the same substrate/solution ratio. Substrate EC and pH are presented in Table 1.

PLANT MATERIALS

Whole specimens of selected grass and dicotyledonous plant species that grow spontaneously were collected in the close vicinity of the tailings pond and from the zone of eolian transmission of waste particles. The following plant species were investigated: *Cardaminopsis arenosa* (L.) Hayek, *Calamagrostis epigeios* (L.) Roth, *Deschampsia caespitosa* (L.) P. Beauv., *Festuca ovina* L., *Silene vulgaris* (Moench) Garcke and *Viola tricolor* L. Three root preparations were made for each sampled plant collected from sites A, B and C; 54 samples were used for analysis. In addition to plant material, substrate samples from outside the root systems were collected as bulk substrate.

ANALYTICAL METHODS

Root pieces 2.0–2.5 cm long with particles of substrate adhering to them were fixed to aluminum stubs with double-sided carbon tape immediately after collecting. The substrate adhering to the root surface (rhizosphere substrate) and the root surface were treated as the rhizosphere.

Using a stereomicroscope, a few hundred particles of bulk substrate representative of each sample were selected for analysis and placed on carbon adhesive tape.

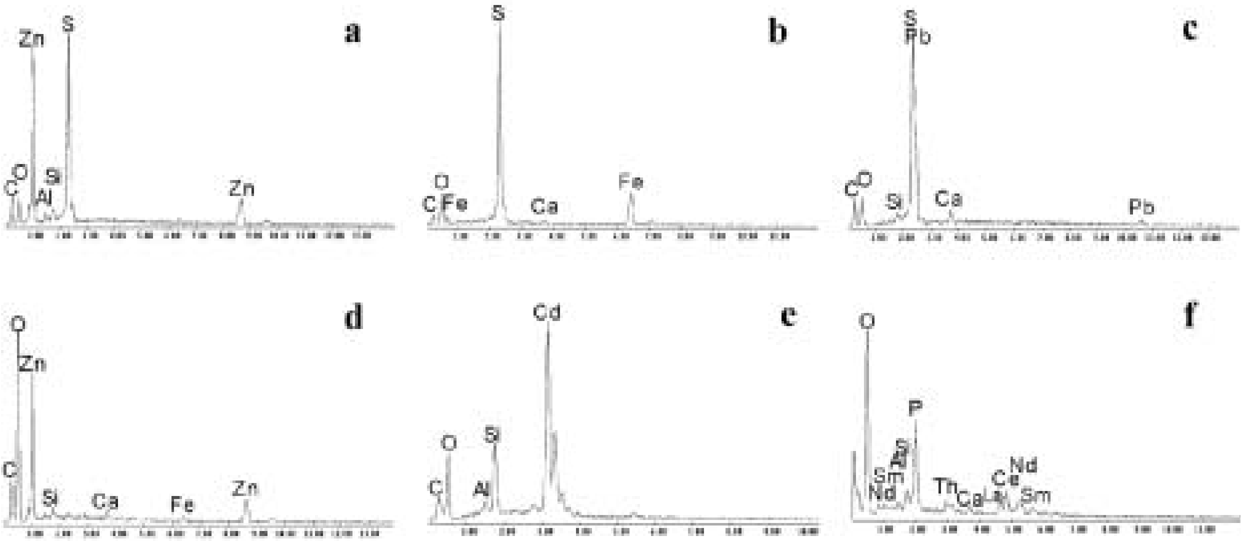


Fig. 3. EDS spectra of identified chemical compounds. (**a**) Zn sulphides, (**b**) Fe sulphides, (**c**) Pb sulphides, (**d**) Zn carbonates, (**e**) Cd carbonates, (**f**) Ce, La phosphates with RRE.

Electron-probe microanalyses and observations were performed with an environmental scanning electron microscope (ESEM; Philips XL 30, Netherlands) with an EDAX analyzer.

An ESEM with a back-scattered electron (BSE) detector (Centaurus, Great Britain) was used to view 54 plant samples and 54 bulk substrate samples, uncoated. An attached EDAX (Sapphire, Netherlands) energy dispersive X-ray spectrometer was used to perform 500 qualitative microanalyses (EDS) of plant material and 192 microanalyses of bulk substrate. Experimental conditions: accelerating voltage 15 kV, environmental mode, H_2O pressure 0.2 torra. To document the analyzed objects, 84 BSE images of plant specimens and 84 of bulk substrate material were registered.

The composition of the examined materials was determined by the presence of characteristic peaks of some elements in the analyzed EDS spectra (Fig. 3). Figure 4 shows the frequencies of mineral classes recognized on the plant roots based on 500 analyzed grains.

MINERALS OF WASTE FROM ORE PROCESSING AND OF SUBSTRATE FROM THE SURROUNDINGS OF THE TAILINGS POND

Owing to their location as well as the mineral and granulometric composition of the stored material, tailing ponds are the most important source of metallic substances occurring in local soils.

Run-of-mine ore undergoes crushing and grinding. The slurried product from the grinding mills passes to flotation circuits. The waste material is fine-grained with unflotable and/or low-flotable particles smaller than 0.04 mm in diameter. Gangue minerals comprise about 90% of mine output (Cabała, 2001; Górecka et al., 1994). Apart from clay minerals (mostly Fe, K and Mg aluminosilicates) and the carbonates dolomite $CaMg(CO_3)_2$, ankerite $Ca,Mg,Fe(CO_3)_2$ and calcite $CaCO_3$, there are the sulphides pyrite and marcasite FeS_2 (up to 14.6%), sphalerite ZnS and galena PbS (about 1%) together with the sulphate barite $BaSO_4$, occurring as primary minerals in the material stored in tailings ponds. Iron oxides and hydroxides (both amorphous phases and goethite) as well as the unstable hydrated sulphates melanterite $FeSO_4 \cdot 7H_2O$, rozenite $FeSO_4 \cdot 4H_2O$, copiapite $Fe_5(SO_4)_6(OH)_2 \cdot 20H_2O$, epsomite $MgSO_4 \cdot 7H_2O$ and hexahydrites $(Mg,Zn,Fe)SO_4 \cdot 6H_2O$ are the most frequent secondary minerals found. Gypsum $CaSO_4 \cdot 2H_2O$ and jarosites $KFe_3[(OH)_6/(SO_4)_2]$ are the main stable sulphates observed among secondary minerals. The secondary carbonates smithsonite $ZnCO_3$ and cerussite $PbCO_3$ are less common (Żabiński, 1964; Kucha and Jędrzejczyk, 1995; Cabała, 2001). Mineral components of Zn-Pb ore flotation tailings are shown in Figure 2. Flotation waste- impacted soils in the area concentrate high quantities of Zn, Pb, Cd, Fe and other heavy metals (Gruszczyński et al., 1990).

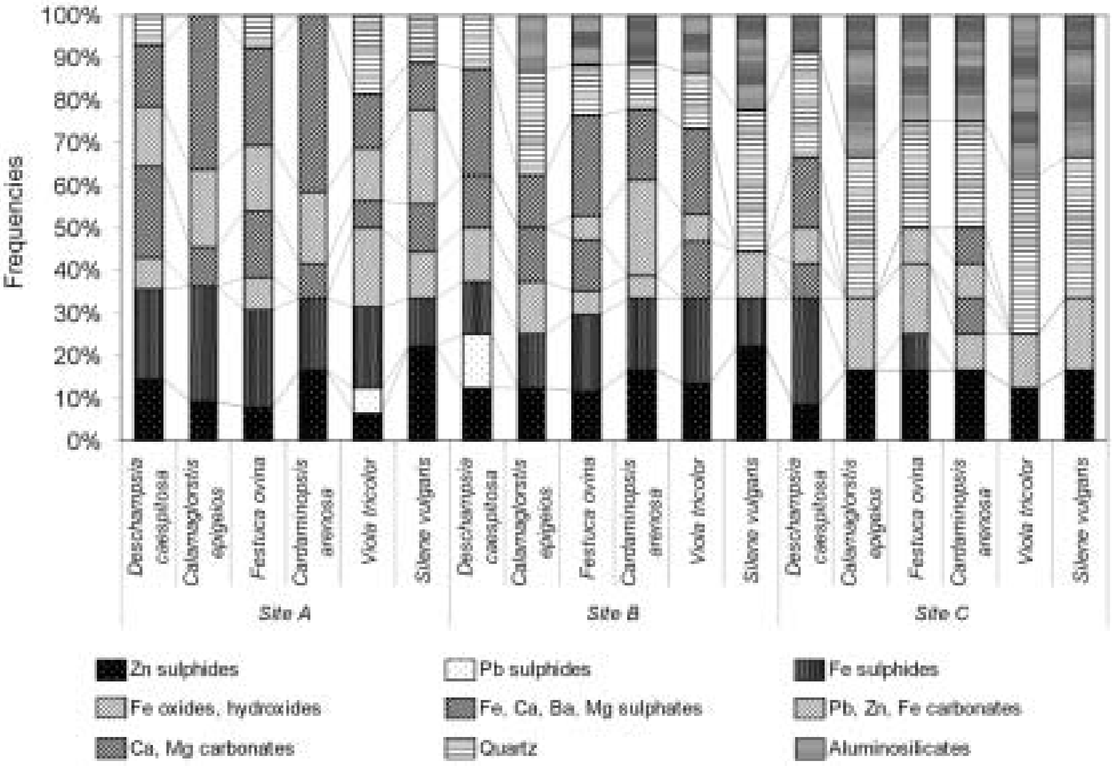


Fig. 4. Frequencies of mineral classes on examined roots, by plant species and sampled sites, based on 500 qualitative microanalyses.

RESULTS

Apart from the parental mineral components of the substrate, allochthonous minerals were found in the examined material, which could have come into the rhizosphere from Zn-Pb ore flotation tailings ponds, atmospheric dustfall, or dustfall related to local industrial emissions.

Certain minerals were identified by determining crystal chemistry in EDS analyses of the rhizosphere and correlating the data with observations of crystal morphology. The sulphides found included sphalerite and wurtzite ZnS (Fig. 3a), pyrite and marcasite FeS_2 (Fig. 3b), and galena PbS (Fig. 3c). Other minerals were dolomite $CaMg(CO_3)_2$, cerussite $PbCO_3$, smithsonite $ZnCO_3$ (Fig. 3d), otavite $CdCO_3$ (Fig. 3e), gypsum $CaSO_4 \cdot 2H_2O$, barite $BaSO_4$, quartz SiO_2, zircon $ZrSiO_4$, apatite $Ca_5[(F, OH)|(PO_4)_3]$ (Fig. 3f), monazite $Ce(PO_4)$ and asbestos. When the EDS results were ambiguous or insufficient for correct identification, mineral components could only be assigned to chemical classes: aluminosilicates (clay minerals, feldspars), sulphates and oxides. The main parental components of the soils were quartz together with K, K-Na and Na aluminosilicates, accompanied by accessory minerals originated in quartz sands.

Ore minerals recognized in both the rhizosphere and bulk substrate (Tab. 2) coexisted in the same genetically coherent assemblages (parageneses) as those known from the waste pond (Fig. 5). The ore mineralization content away from the pond (sites B and C) was usually higher in the rhizosphere than in bulk substrate (Tab. 2), reaching a maximum 3%.

More than 50% of the root surface was coated with polymineral associations aggregating sulphides, oxides and aluminosilicates (Fig. 6). Mineral envelopes formed where roots branched off (Figs. 5, 7).

Zinc, lead and iron sulphides were found everywhere in the rhizosphere of the analyzed plants. Zn and Pb carbonates were less frequent. Pyrite and marcasite grains occurring on the roots reached up to 200 µm in size, and their surface was abundant with crystalline and/or amorphous sulphates produced by oxidation of iron sulphides (Fig. 5). Unstable Fe, Mg and Ca sulphates (Fig. 7) could grow in their true (automorphic) crystalline complexion directly at the root surface. Crystalline iron oxides produced by Fe sulphide oxidation were noted in the

TABLE 2. Groups of primary and secondary minerals determined in bulk substrate and rhizosphere of examined plants

Group of minerals	Site A		Site B		Site C	
	Rhizosphere	Bulk soil	Rhizosphere	Bulk soil	Rhizosphere	Bulk soil
Zn sulphides	+	+	+	+	+	+
Pb sulphides	+	+	+	+	+	+
Fe sulphides	+++	+	+++	+++	+	+
Fe oxides, Fe hydroxides, Mn oxides	+++	+	+	+	+	+++
Fe sulphates, Zn sulphates, Pb sulphates	+	+	+	+	+	
Ca, Mg sulphates	+				+	
Ba sulphates	+	+	+	+		+
Pb carbonates, Zn carbonates, Fe carbonates	+	+	+	+	+	
Cd carbonates					+	
Ca carbonates, Ca,Mg carbonates	+++	+++	+	+	+	+
Zn silicates				+		+
Quartz	+	+	+	+++	+	+++
K aluminosilicates, K,Na aluminosilicates		+	+	+	+++	+
Accessory minerals: Ce,La phosphates with RRE, Zr silicates, Ti oxides, Asbestos	+				+	

+ – relative frequency based on counting mineral grains in analyzed samples

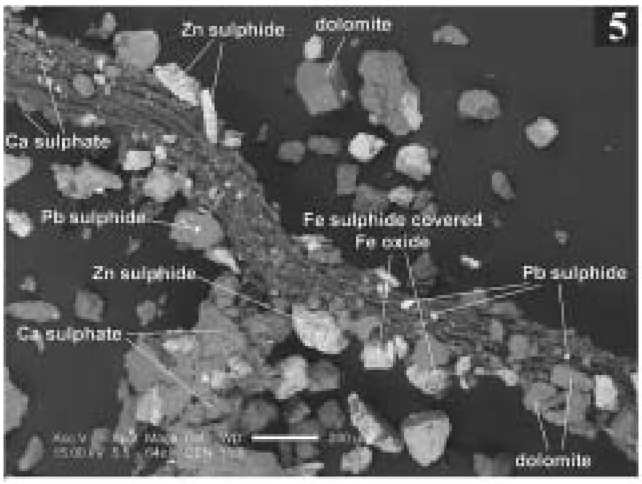
rhizosphere (Fig. 8). The secondary sulphates and crystalline iron oxides present in the rhizosphere suggest that oxidation dominates reduction in this soil compartment more than in bulk substrate.

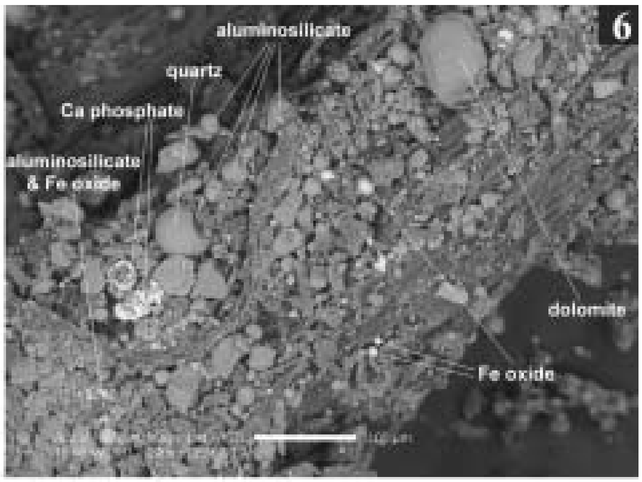
Aggregates of gypsum were observed overgrowing the root tissue in situ (Figs. 5, 7), formed when calcium ions were released by the dissolution of carbonates (calcite and/or dolomite), and the dissolution and oxidation of sulphides formed sulphate ions.

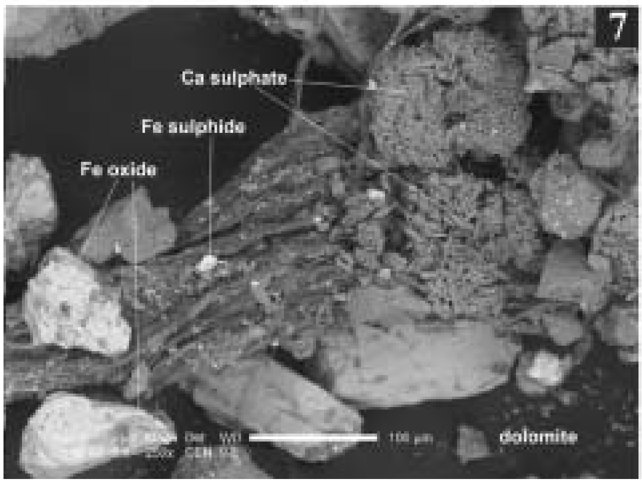
The rhizosphere of plants growing away from the tailings pond is a low-Fe sulphide environment, as primary iron sulphides were replaced there by secondary iron oxides (Fig. 8). In many cases the secondary iron minerals assumed concentric or spheroidal shapes (Figs. 8, 9). Some of the spherulites were made up of polymineral mixtures composed of iron oxides and aluminosilicates (Fig. 6). Spheroidal forms consisting exclusively of clay minerals were also documented (Fig. 8). The spherulites presumably were nucleated while undergoing weathering processes in the rhizosphere with oxidation conditions prevailing.

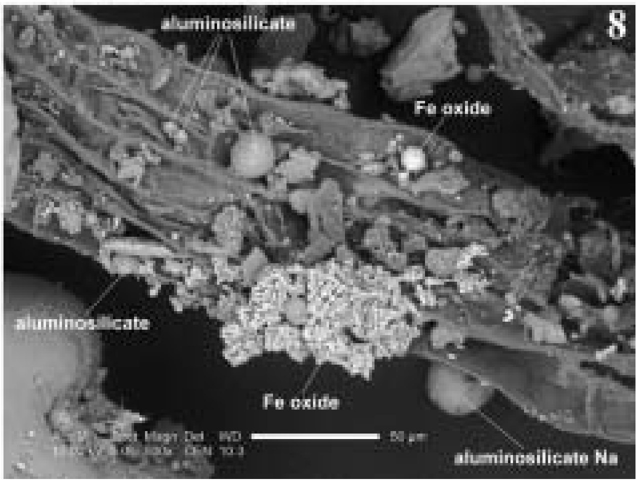
Figure 4 shows that the frequencies of some mineral classes in rhizosphere depended on the distance from the pollution source. Samples from distant places (sites B and C) contained more quartz and aluminosilicate grains as well as iron oxides and hydroxides than from site A, and less iron sulphides and Ca and Mg carbonates than from site A. Zn, Pb and Fe carbonates appeared mostly at site A. Their occurrence in sites B and C was irregular; the roots of certain species (*Cardaminopsis arenosa, Festuca ovina, Viola tricolor*) apparently abounded with them (Fig. 4).

At this point of the research it is difficult to say unequivocally whether the mineral composition of the rhizosphere differed depending on the examined species, but preliminary observations indicated that the soil on roots of *Cardaminopsis arenosa, Viola tricolor* and *Festuca ovina* was richer in zinc and lead carbonates than the bulk substrate. Moreover, fine (2.5 µm) grains of Cd carbonate were found at site C in the rhizosphere of *Cardaminopsis arenosa* (Fig. 3e). The crystalline shape of this secondary mineral of cadmium suggests a form of otavite $CdCO_3$. As cadmium carbonates have not been found previously in Zn-Pb orefields of the Silesia-Cracow district, the occurrence of otavite-like mineral in the rhizosphere is thought to be an effect of root system activity. Other secondary minerals identified on the examined plant roots indicate that local release of ions such as SO_4^{2-}, Fe^{3+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+} and Mn^{4+} can also occur in the rhizosphere.









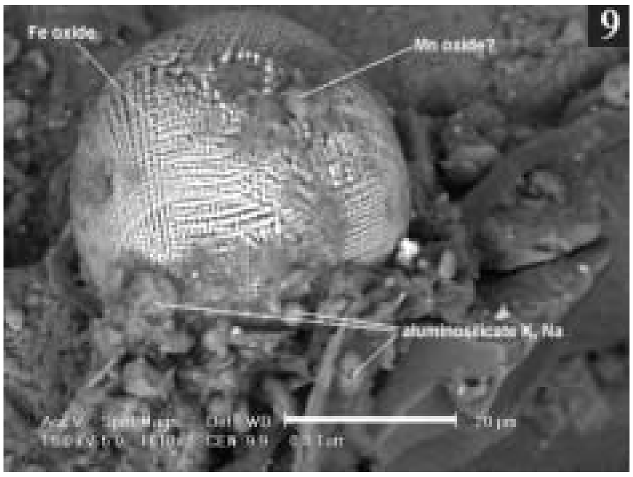


Fig. 5. *Deschampsia caespitosa* roots (site A). **Fig. 6.** *Viola tricolor* roots (site C). **Fig. 7.** *Deschampsia caespitosa* roots (site A). **Fig. 8.** *Calamagrostis epigeios* roots (site C). **Fig. 9.** *Cardaminopsis arenosa* roots (site B).

DISCUSSION

The mineral composition of the examined rhizosphere substrate corresponds with the mineralogy of Zn-Pb ore processing waste (Kucha and Jędrzejczyk, 1995; Górecka et al., 1994). The assemblages of secondary minerals we found in the bulk substrate are remarkably similar to the mineral sequences (parageneses) that result from natural weathering of MVT zinc-lead deposits (Żabiński 1964; Cabała, 2001; Leach et al., 2001; Mayer et al., 2001).

Plant roots can modify their environment (rhizosphere) by changing soil pH, lowering or enhancing the soil redox potential, or releasing different organic compounds (Marschner and Römheld, 1996; Gobran et al., 1998). In the present study the amounts of sulphates and/or carbonates were higher in the rhizosphere of examined plants than in bulk substrate. Crystalline iron oxides were also produced by FeS_2 oxidation in the rhizosphere (Tab. 2). It was documented that uptake of Fe^{2+} ions by all plant species is correlated with the reduction activity of plant root systems (Curie and Briat, 2003). However, the sulphates, carbonates and crystalline iron oxides observed in the rhizosphere (Tab. 2; Figs. 7, 8) suggest that oxidation processes dominate over reduction processes in the rhizosphere of the investigated plant species. Spheroidal forms of secondary iron minerals (Figs. 8, 9) also could be formed in the rhizosphere where oxidation conditions prevail. Polymineral spherules present in the rhizosphere (Fig. 6), originating as a result of chemical weathering, evidence chemical activation of iron oxides and sheet aluminosilicates under weathering conditions. Courchesne and Gobran (1997) also documented more intensified weathering of minerals in the rhizosphere than in bulk soil. They observed depletion of weatherable minerals (e .g., amphiboles) and concomitant accumulation of amorphous inorganic and organically complexed Al and Fe in the rhizosphere of Norway spruce (*Picea abies*); they did not investigate the redox potential in the rhizosphere, however. The effect of oxidation or reduction conditions on the formation of secondary iron minerals in the rhizosphere should be examined further.

Clay minerals and Fe oxides exhibit high sorptive capacity with reference to heavy metals (Kabata-Pendias, 1980). As the sorption surface of spheroidal and skeletal aggregates of iron oxides (Figs. 6, 8 and 9) is even larger than on grains of other crystal habits, the presence of such mineral intergrowth patterns can profoundly affect local chemical changes in the analyzed rhizosphere.

Plants release into the rhizosphere H^+ ions and organic acids, which can acidify the rhizosphere soil even two units below that of the bulk soil (Marschner and Römheld, 1996; Gobran et al., 1999 and literature therein). In such conditions, Ca carbonates (calcite, dolomite) can be easily dissolved and release Ca^{2+} ions. On the other hand, the high redox potential in the rhizosphere can lead to formation of sulphate ions by dissolution and oxidation of sulphides. The gypsum aggregates we observed in the rhizosphere (Figs. 5 and 7) were likely formed as a result of dissolution of carbonates and oxidation of sulphides by plant root systems.

Some plant species, called hyperaccumulators, accumulate certain heavy metals to extremely high, normally toxic concentrations in their shoots (Małkowski and Kurtyka, 2003). *Cardaminopsis arenosa*, similarly to the Zn and Cd hyperaccumulator *Cardaminopsis halleri* (Küpper et al., 2000), probably belongs to this group of plants. We found fine grains of Cd carbonate in the rhizosphere of *Cardaminopsis arenosa* from site C (Tab. 2; Fig. 3e). This secondary mineral of cadmium was considered to be otavite $CdCO_3$. As cadmium carbonates were not found previously in Zn-Pb orefields of the Silesia-Cracow district, the occurrence of otavite-like mineral in the rhizosphere should be an effect of root system activity. Since $CdCO_3$ was not found in the rhizosphere of other investigated plant species, which are nonaccumulator plants, the formation of Cd carbonates might be connected with the phenomenon of tolerance and/or hyperaccumulation of Cd by *Cardaminopsis arenosa*. This result is striking, because it was documented that root exudates of *Thlaspi caerulescens*, another hyperaccumulator plant species, did not significantly enhance mobilization of Cd and therefore are not involved in Cd hyperaccumulation (Zhao et al., 2001). Further research is needed to elucidate this problem.

Gobran et al. (1998) analyzed rhizosphere properties and processes in forest soil. They reported that decomposition, dissolution and precipitation of soil minerals due to root and associated microorganism activity is more enhanced in the rhizosphere than in bulk soil (Gobran et al., 1998). Our results also showed that plant roots affected the mineralogical composition of substrate from the surroundings of a Zn-Pb ore flotation tailings pond. It cannot be ruled out that the changed mineral composition in the rhizosphere substrate observed in the current study is due in part to the activity of rhizosphere microorganisms.

Some minerals (Zn, Pb, Cd, Tl) were very close to the root surface or in hollows of roots of the investigated plant species. Such minerals could be difficult to remove during preparation of plant material for analyses and could affect the final concentrations of metals in dry weight.

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