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Original Research

Mineral Composition of Atmospheric Dust in Biebrza National Park, Poland

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Abstract

Biebrza National Park (BNP) in NE Poland is one of the least polluted regions of Europe and as such seems to be well suited for the determination of the composition of natural-background pollution of atmospheric dust. Samples of fallen dust were collected at monthly intervals between April 2003 and March 2004 in the isolated settlement of Grzędy. X-ray powder diffraction, scanning electron microscope images, and energy dispersive spectrometry revealed quartz, feldspars, micas, kaolinite, chlorite and hematite as major dust constituents. In addition, a few grains of Ni, Ni-Fe phosphide, and Fe-Ni-Cr oxides (probably of extraterrestrial origin) were observed. Anthropogenic constituents include amorphous aluminosilicates, barite, gypsum, Sn, Fe, Ti and Bi-W oxides. Quartz and feldspars constitute the majority of natural-dust pollution in BNP. Both grain size and mineral composition exhibit seasonal variations.

Keywords: background dust pollution, atmospheric dust, Biebrza National Park

Introduction

Knowledge of the compositions of atmospheric dust is pertinent to understanding its impact on human health. One of the challenges in studying air pollution is to distinguish between pollutants emitted from natural sources and those of anthropogenic origin. Natural dust particles form background pollution on which anthropogenic dust particles can be superimposed. Global estimates show that more than two thirds of dust pollution originates from natural sources, *i.e.* rock and soil erosion, sea sprays, volcanism, forest fires, and biogenic activity [7]. The annual flux of natural particles smaller than 20 µm ranges from 1390 to 2109 Tg against 421-614 Tg of dust particles emitted from anthropogenic sources [7].

Previous investigations of the phase composition of atmospheric dust in Poland focused on industrial regions, mainly Upper Silesia and Cracow, which have always been predominant contributors to total dust emission in the country [1-4]. In those regions dust particles from anthropogenic sources predominate over natural constituents of the dust. Even in protected areas of Southern Poland, such as the Tatra Mts. and Niepołomice Forest, numerous phases related to emissions from heavy industry, domestic coal-burning, and transportation were identified [5, 6]. Despite the dramatic decrease in dust emission in Poland since 1990, *i.e.* after the political and economic transformations which caused the industrial production decline and improvement in environmental protection, the anthropogenic phases still remain major constituents of airborne dust in industrial and heavily urbanized regions. Therefore, it is difficult to determine the composition of natural background pollution of atmospheric dust in that part of Poland.

In this study, we report the results of a mineralogical investigation of fallen atmospheric dust (particles with diameters <300 (m) collected between April 2003 and March 2004 in Biebrza National Park in NE Poland (Fig. 1). BNP is considered pristine and is the least polluted

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*Corresponding author; e-mail: mjablons@us.edu.pl part of Poland, making it suitable for the determination of natural-dust pollution.

The sampling site was located in the remote northern part of BNP, near the isolated small settlement of Grzędy (Fig. 1) (N=53°37′56″; E=22°46′21″). The nearest town, Grajewo, with a population of 20,000, is situated some 20 km west of the sampling site in the direction of prevailing downwinds. The annual concentration of airborne dust particles PM10 (particulate matter of aeordynamical diameters <10 (m) in Grajewo was as low as 6.5 μg·m^{-3} in 2002 [8], an order of magnitude lower than in Upper Silesia. The major dust sources in Grajewo and Augustów (Fig. 1) are local heat-generating plants.

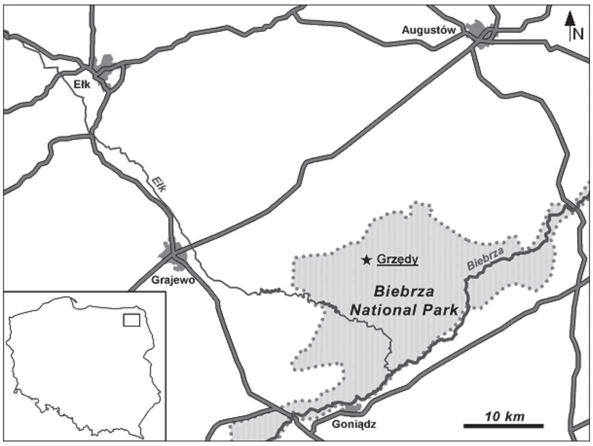

Fig. 1. Location of dust sampling site (Grzędy) in the Biebrza National Park, Poland.

Experimental Procedures

Samples of dust were collected in glass jars (volume $1·10^3$ cm^3 and overall surface area $5·10^{-3}$ m^2) at monthly intervals between April 2003 and March 2004. The jars were placed 2 meters above the ground. The mass of samples of fallen dust ranged between 0.26-2.00 g·m^{-2} per month. We observed seasonal variation in the amount of dust depending mainly on plant vegetation.

All samples were examined by X-ray powder diffraction (XRD) using a Phillips PW 3710 diffractometer. The operating conditions were: Cu-Kα_1 radiation graphite monochromator, voltage 45 kV, current 30 mA, counting time 8 sec and scan rate 0.01°.

The samples were also examined using scanning electron microscopy (SEM) with a Phillips XL30 ESEM TMP operated at 15 kV accelerated voltage, current 20 nA, diameter of electron beam 2 μm, spot size 5, CENTAURUS detector and equipped with an EDAX EDS Sapphire system.

Dust particle size was measured in two dimensions using a calibrated SEM (automatical measurement function of real distance selected objects). Particulate diameters were determined as a root-mean-square size (r.m.s.=$\{a^2+b^2\}^{1/2}$), where *a* and *b* are two orthogonal directions across the grain [3].

Table 1. Major inorganic components and their size distribution of fallen dust from Grzędy, Poland.

Component	Content [%vol]	Size distribution [% vol]			
		<5 μm	5-10 μm	10-50 μm	>50 μm
quartz:					
summer season samples	15-24	3	21	60	16
winter season samples	17-30	22	39	30	9
aluminosilicates:					
summer season samples	35-50	25	32	29	14
winter season samples	15-27	7	14	59	20
iron oxides and hydroxides:					
summer season samples	14-26	30	26	28	6
winter season samples	17-37	40	21	25	14
carbonates:					
summer season samples	0-6	40	29	15	16
winter season samples	17-24	31	35	34	0
all particles:					
summer season samples		25	21	44	10
winter season samples		30	31	30	9

Results and Discussion

In this study, we define a major component as one that is at least 5% of the sample's volume and usually, if crystalline, can be detected by X-ray powder diffraction. Major phases identified in all samples, regardless of the season, include quartz, various crystalline and amorphous aluminosilicates and iron oxides and hydroxides. In winter, Ca, Mg-Ca and Fe-Ca carbonates and barite occurred in significant amounts, up to 24 and 5 vol%, respectively (Table 1).

Quartz is the most abundant phase in all samples, amounting to 30% by volume. Quartz grains are angular or rounded. Their sizes range from a few to 50 μm in diameter, though particles up to a few hundred μm in diameter were observed.

The group of aluminosilcates contains both crystalline and amorphous components and together they constitute up to 27 vol% in summer and up to 50 vol% in winter. Crystalline aluminosilicates include potassium feldspars, plagioclases, unidentified micas, kaolinite and chlorites. Those aluminosilicates occur usually as angular or semirounded grains and contain K, Mg and Fe in significant amounts. Their diameters range from a few to tens of μm. Fibrous Ca, Na, Mg and Fe-bearing aluminosilicates, most probably glass fibers, were also observed. They are 100-500 μm long and their diameters range from 1 to 5 μm.

Table 2. Minor inorganic components and their observed size range of fallen dust from Grzędy, Poland.

component	vol%		observed size range [μm]
	summer season samples	winter season samples	
sulphates:			
barite	0-2	0-5	1-10
gypsum	not detected	0-0.5	20-30
sulphides:			
pyrite	independent of season 0-0.5		1-2
galena	0-1	not detected	2-10
oxides:			
Ti oxide	0-4	not detected	3-20
Sn oxide	0-3	not detected	2-12
ilmenite	not detected	0-3	20-70
salts:			
sylvite	0-3	not detected	5-20
halite	not detected	0-2	
phosphates:			
apatite	independent of season 0-2		2-5
REE phosphates	independent of season 0-2		3-8
Bi-W oxide	0-2	not detected	2-8
Fe-Ni phosphide	0-1	not detected	1-4
Fe-Ni-Cr oxides	0-1	not detected	5-15

Amorphous aluminosilicates are distinguished from crystalline ones by spherical shape of their particles, small size (diameter < 5 μm) and enrichment in Fe, Ti, Mg, Ca and Na. They resemble the prevalent aluminosilicates observed in dust in Upper Silesia, which were coal combustion products [9].

Iron oxides and hydroxides are abundant in all samples. Angular grains predominate, although spherical particles are also common. Sizes of the particles range from a fraction of μm to more than 100 μm. However, particles no longer than 5 μm were predominant both in summer and winter. X-ray powder diffraction detected the presence of iron oxides – hematite and magnetite (Fig. 2).

Among the minor dust-particle phases listed in Table 2, REE-phosphates (Fig. 3), Sn oxide (Fig. 4) and Bi-W-oxide are exotic**.** In samples collected in August and September of 2003 a few particles of Ni, Ni-Fe phosphide (Fig. 5a, b) and Ni-Fe-Cr oxide were found (Fig. 6). Ni phosphide, with Fe in solid solution (Ni, Fe)$_3$P) is unknown from terrestrial materials but occurs in meteorites [11]. While we did not study abundant organic particles (mainly pollens and diatoms), we noticed that some of them adsorbed metals on their surfaces (Fig. 7).

Both grain size and mineral composition exhibit seasonal variations. Samples of dust collected during summer showed a bimodal grain-size distribution characterized by particles with diameters less than 5 μm (25 vol%) and in the range of 10 to 50 μm (44 vol%). Coarser-grained particles have diameters larger than 50 μm and constitute only about 10 vol% (Table 1). In samples collected during winter, about 30 vol% of the particles had a diameter in the range of 10-50 μm. Coarse-grained particles form only 9 vol% of the total dust load and 60 vol% of the particles had diameters smaller than 10 μm.

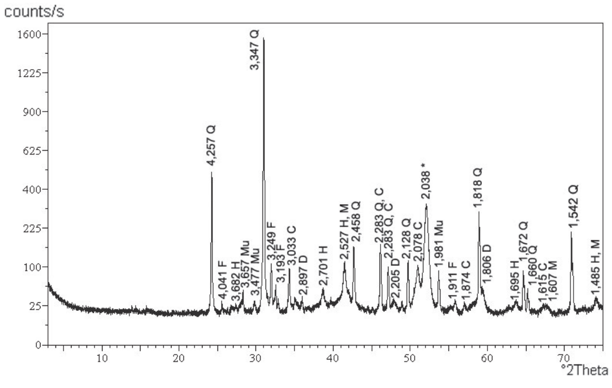

Fig. 2. X-ray powder diffraction pattern of fallen dust from Grzędy, Poland. Q – quartz, C – calcite, D – dolomite, F – feldspars, H – hematite, M – magnetite, Mu- muscovite. 2.038* peak is an experimental artifact (underlying metal target).

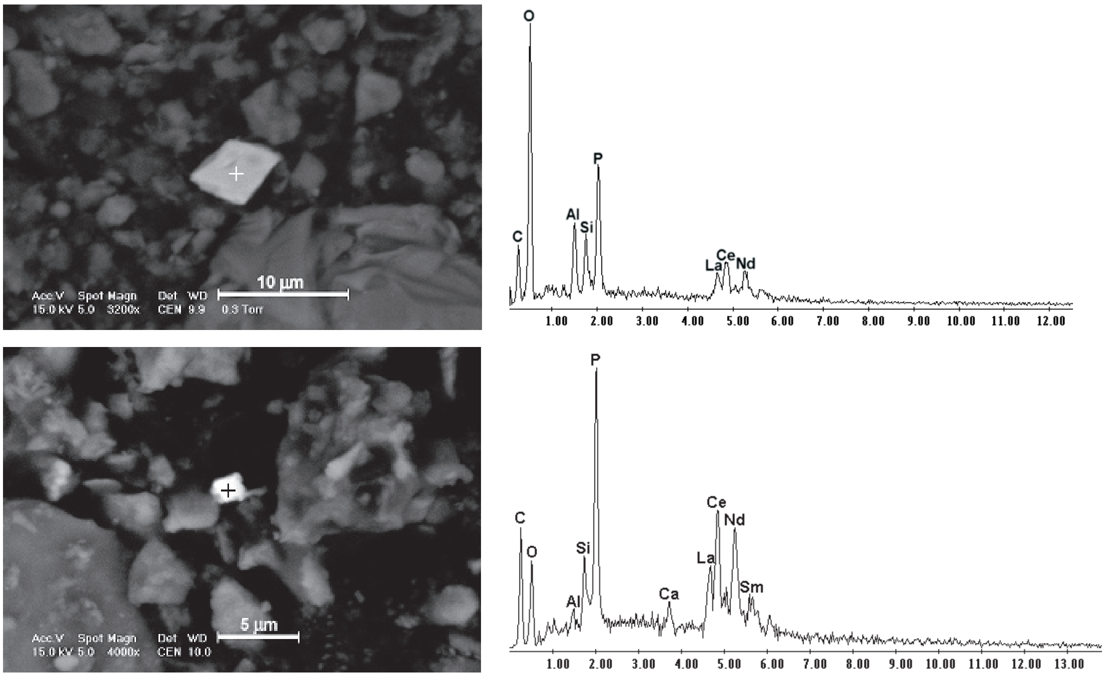

Fig. 3. SEM images and EDS spectra of REE phosphates in dust particles from Grzędy, Poland. The C peak is an experimental artifact (carbon tab), Al and Si peaks are from surrounding particles.

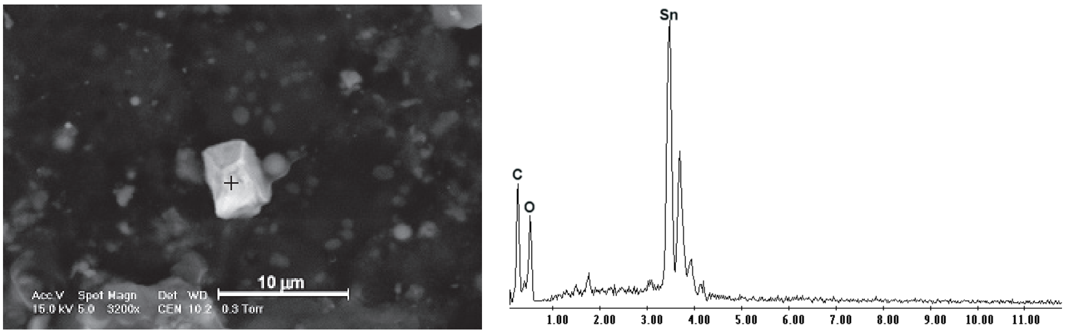

Fig. 4. SEM image and EDS spectrum of Sn oxide in dust particles from Grzędy, Poland. The C peak is an experimental artifact (carbon tab).

The abundance of barite and carbonates in samples collected during winter characterize the most conspicuous seasonal variation in mineral composition. Barite euhedral crystals are abundant in atmospheric dust over Upper Silesia as a result of the burning of Ba-enriched Upper Silesian coals [3, 11]. Barite particles collected in BNP are always angular. This feature suggests that barite was released during low-temperature coal combustion. High-temperature coal combustion decomposes pristine barite into BaO, which reacts with sulphuric aerosol to form crystals of secondary-airborne barite [3].

Unlike in Upper Silesia, the amount of gypsum in BNP is negligible. Gypsum forms when sulfuric acid aerosol reacts with airborne Ca-rich dust. In Upper Silesia and its environs, gypsum occurs in such large concentrations that it can easily be detected by X-ray powder diffraction [4]. The abundance of carbonates in winter dust in BNP suggests that that reaction did not occur on a large scale; otherwise carbonates would have reacted with sulfuric acid to form gypsum [3]. In this respect, it is interesting to note that rainfall acidity during the winters of 2003 and 2004 in BNP was lower than during the spring and summer (W. Krawczyk, pers. comm., 2005). The acidity of rain in BNP from May (pH = 3.33) till August (pH = 4.91) of 2003 was high with a minimum pH of 2.99, recorded in July. The rain and snow acidity decreased during heating period from pH=5.88 in September to pH=7.41 in November (W. Krawczyk, pers. comm., 2005). The concentration of airborne dust over BNP is too low to explain such dramatic changes in the acidity of rainfalls by neutralization reactions.

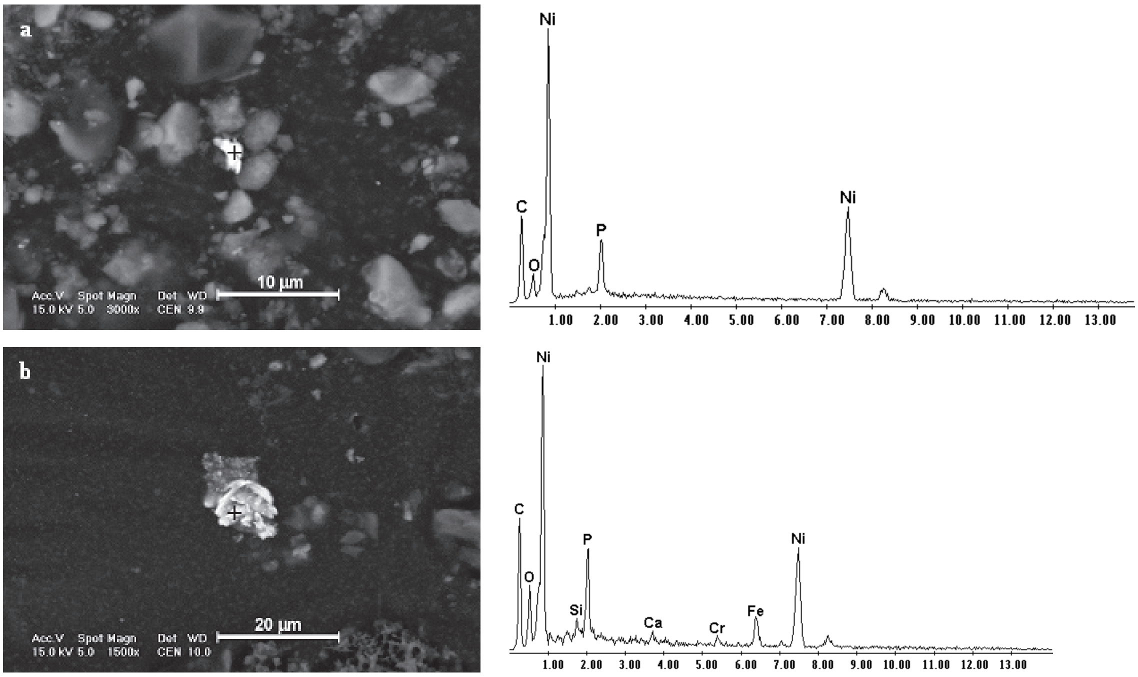

Fig. 5. SEM images and EDS spectra of nickel phosphide (a) and Fe, Cr-bearing nickel phosphide (b) in dust particles from Grzędy, Poland. The C peak is an experimental artifact (carbon tab), Ca, Si and O peaks may be from surrounding area.

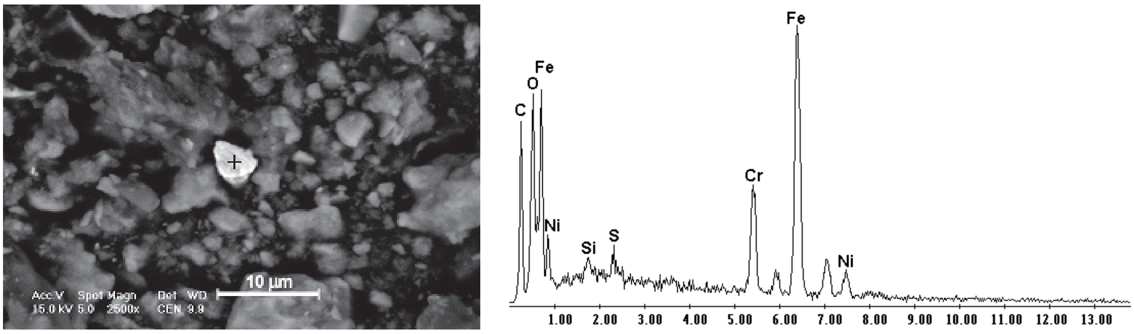

Fig 6. SEM image and EDS spectrum of Ni-Fe-Cr oxide in dust particles from Grzędy, Poland. The C peak is an experimental artifact (carbon tab), Si and S peaks are from surrounding particles.

Conclusions

Seasonal changes in the mineral composition of dust deposits are linked to human activities such as burning fossil fuel, mainly coal. However, most major dust constituents in BNP are natural, regardless of the season. Quartz, crystalline aluminosilicates (feldspars, micas, kaolinite) and some iron oxides and hydroxides were derived from the weathering and erosion of rocks and soils. They occur in dust deposits as a result of both short-range and long-range transport (more than 1000 kilometers). These phases are common constituents of natural atmospheric dust [12]. Possibly, some quartz may be released into the atmosphere during coal combustion. Amorphous silica and aluminosilicates and some iron oxides and hydroxides are certainly anthropogenic [13, 4]. Spherical Fe-Mg-Ti-Ca-Na-bearing aluminosilicates are typical of fly ash [14, 9, 3].

The origin of dust particles containing REE is problematic. REE in Upper Silesian coals may have been released during coal combustion. On the other hand, they commonly occur in Quaternary soils.

Semi-quantitative analysis of inorganic dust deposits in BNP suggests that natural components predominate over anthropogenic ones. This is not unexpected since BNP is one of the least polluted regions in Poland. Perhaps this fact contributed to the detection of extraterrestrial nickelphosphide in one of the samples. However, even in BNP, the anthropogenic imprint of atmospheric dust can be distinguished due to the presence of anthropogenic constituents such as glass fibers, amorphous aluminosilicates, barite, and metal alloys.

We are aware of the fact that mineralogical composition of nanoparticles may be slightly different from microparticles observed during this study. Nevertheless, we

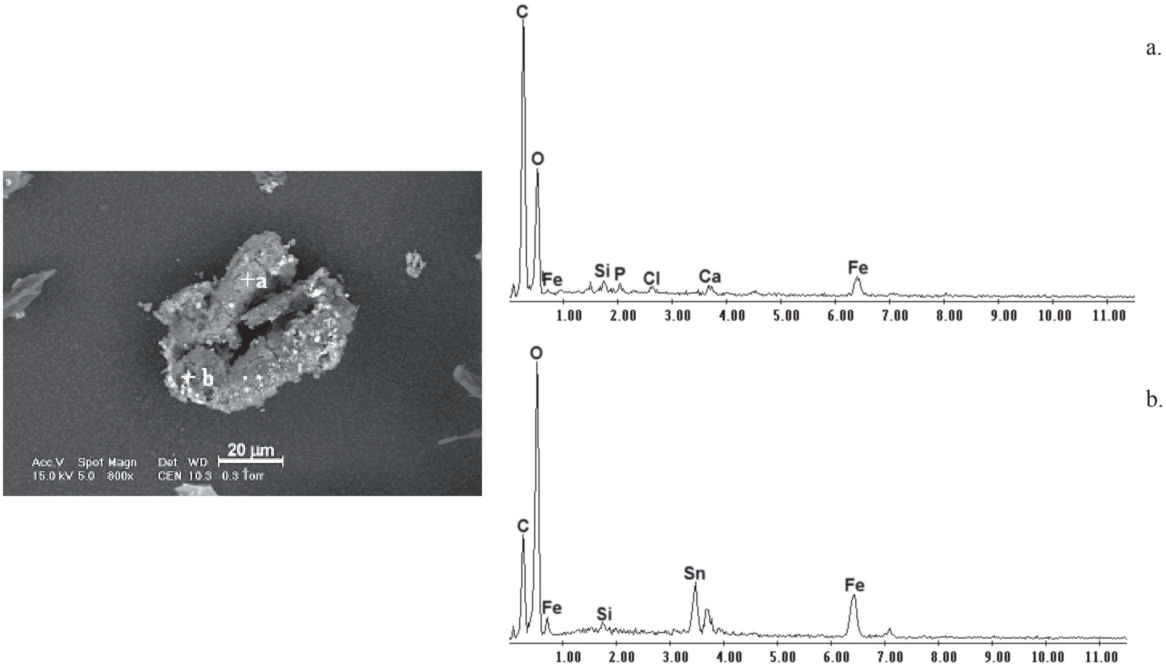

Fig. 7. SEM image and EDS spectra of organic particle (a) with adsorbed metals (Sn, Fe) (bright spots) (b) in dust particles from Grzędy, Poland. The C peak is an experimental artifact (carbon tab).

conclude that quartz and especially feldspars can be used to semiquantitatively determine the natural background of atmospheric dust pollution.

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