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Chemical and Phase Structure of Technogenic Aerosols in the Region of the Siberian Chemical Plant (Tomsk Region)

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Abstract

Results of the study of aerosols in the region of the Siberian chemical combine (Seversk, Tomsk Region) performed in 2010 using scanning electron microscopy and X-ray diffractometry are given. GIS methods allowed revealing features of the spatial distribution of the aerosol contamination. The decrease of sizes of technogenic aerosol particles with the removal from their source was assessed. Mineral phase indicators of the emissions of the Siberian Chemical Plant (SCP) were determined and their major allocation forms were described.

Key words: technogenic aerosols, rare-earth elements, technogenic minerals, ecological risk

INTRODUCTION

The geoenvironmental problem of the technogenic environmental pollution continues to be relevant. Despite a significant amount of research conducted, the contribution of emissions of large industrial enterprises into the total aerosol pollution in the urbanized territories requires a further study. A special attention should be paid to the emissions of the enterprises of the nuclear fuel cycle (NFC), since the specificity of their production is associated with high ecologic risks.

The snow cover under the conditions of Siberia is the ideal model object to study the composition and dynamics of emissions of industrial plants, since solid aerosol particles in the stable snow cover and gaseous products sorbed on solid phases are registered from the beginning of November until the end of March. Some researchers [1–4] including the author of this work studied geochemical features of the technogenic aerosol pollution in the neighbourhood of Seversk, where the Siberian Chemical Plant (SCP) that is the local economic mainstay of NFC is located. As geochemical indicators of the aerosol pollution, U, Lu, Zn, F, Cs [1, 2] – for the snow cover of Seversk of the SCP, Sr, Eu, Lu [3] – for soil, were determined. As a result of research [4], the list of geochemical indicators of the emissions from the SCP in aerosols was extended: this is not only U but also Th, lithophile Sr, Ba, Y, Nb, Zr, the whole series of rare earth elements (REE). It was established that aerosols of the SCP were enriched with heavy REE with the ratio of (La + Ce)/(Yb + Lu) ~ 28.9. Besides, they are enriched with ^{235}U, by means of which the isotopic ratio of ^{238}U/^{235}U decreases to 74.28 [4].

In 2004–2006, in solid precipitations of the snow cover of the region, a high content of an X-ray amorphous substance, the presence of spherical particles of mullites and magnesioferrites, graphite, asbestos, baddeleyite ZrO_2, uranium oxides UO_2, ferrites, hematites, metallic Au, Pb, Co, Fe, Ni of the technogenic origin, were registered [5]. The same complex of technogenic minerals, except for U oxides, was isolated from soil and soil grounds of the region [6].

The goal of the present work is the study of the occurrence forms of Sr, Ba, Y, Nb, REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in aerosols of the district of the SCP (Seversk).

RESEARCH METHODS

The study was performed using the methods of X-ray diffractometry, electron microscopy with a built-in spectrometer.

Large-volume samples (by 50–70 L) of snow cover in the area of the SCP (Fig. 1) were taken for the collection of a sufficient sample weight of aerosol particles (>300 mg). To exclude the influence of auto roads, sampling points were selected at a minimum distance of 200 m from auto roads. The dustiness (the content of suspended matter) was determined as the ratio of the mass of suspended matters to the volume of melted snow, the dust-aerosol load was defined as the ratio of the mass of suspended matter to the area of selection and duration of existence of the stable snow cover till to the date of sample collection (from November 1, 2009 to March 20, 2010) [4].

The content of soot in aerosols was determined by the way of ashing at 550 °C. The integral phase X-ray structural analysis of incinerated samples was carried out using a DRON-3M powder diffractometer (CuK_α radiation, voltage supplied on the tube $U = 40$ kV, amperage $I = 24$ mA). Using this method one can determine the main mineral-phase composition of samples (containing more than 1–2 %) and evaluate qualitatively their mass fractions.

The morphology and material composition of individual aerosol particles were investigated using a LEO 1430 VP scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS) OXFORD. The diameter of the scanning beam of the spectrometer amounted to ~0.5 μm, which allowed determining the composition of aerosol particles of the size up to 0.5–1 μm. Aerosol particles were deposited by the smooth thin layer onto checkers and studied in the mode of back-scat-

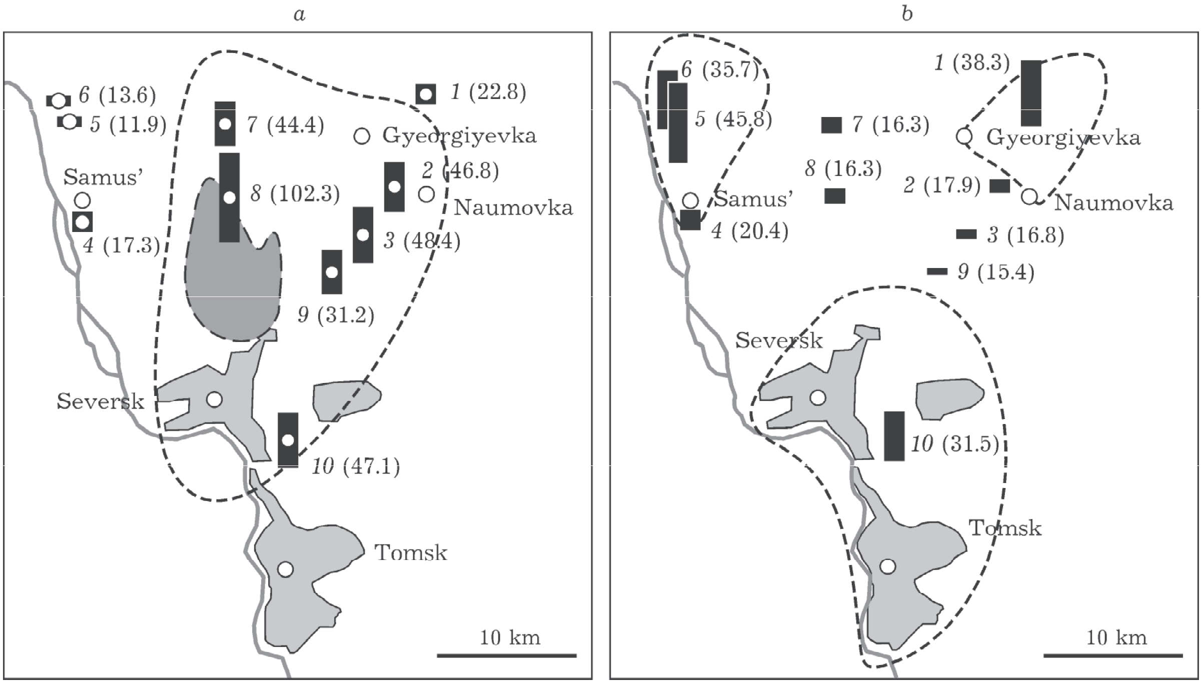

Fig. 1. Location of sampling points of the snow cover in 2010 in the region of Seversk (*1*–*10*). In parentheses: *a* – indicators of dust aerosol load, mg/($m^2 \cdot$ day); *b* – content of soot particles in aerosols, mass %.

TABLE 1

Granulometric composition of aerosols of the region of the Siberian Chemical Plant

Sample No.	Distance from the centre of Seversk, km	Alumosilicate slag spheroids		Soot particles		Fe-containing spheroids		Volume fraction of small particles
		Size, μm	Volume fraction, %	Size, μm	Volume fraction, %	Size, μm	Volume fraction, %	(<20 μm), %
1	27.8	20–50	1	20–150	10	<2–3	0.*n*	90
2	21.0	~50	0.5	50–100	0.0*n*	8–10	0.1	95
		20–50	3	20–50	1	2–5	1	
3	16.9	~50	1	50–100	1	8–10	0.5	88
		20–50	5	20–50	5			
9	13.2	50–120	1	50–100	8	10–25	1	46
		20–50	40	20–50	5			
10	6.85	50–120	25–30	50–100	20	20–40	1–2	40
		20–50	10					

tered electrons under graphite spraying. The evaluation of the volumetric grain-size composition of aerosols was performed using stencils [7]. The search for heavy particles was carried out by the way of decreasing the brightness of the field of view up to the repayment of particles mainly consisting from light elements (particles of soot, aluminosilicate slag spheroids). Herewith, particles consisting of elements with a relative atomic mass ≥56 (heavier than Fe) were isolated by a bright glow, since the higher the atomic mass of the element is, the greater is the reflection of electrons and brighter is the particle. Total, ~7000 fields of survey of the size 212 × 159 μm each that included 300–500 visible aerosol particles of the size of ≥0.5 μm were investigated. The elemental composition of 402 individual aerosol particles, from them, 24 – soot, 68 – aluminosilicate spheroids, 75 – iron-containing spheroids, and 238 – particles containing heavy elements: lanthanides, Y, Zr, Sr, Ba, Au, Ag, Mo, Sn, Pb, Zn, Cu, W, Cr, Co, Bi, Ga was determined.

RESULTS AND DISCUSSION

During the winter period of 2010 at the distance up to 25 km northeast of Seversk, the dust aerosol load amounted to 31.2–102.3 mg/(m^2 · day), on average 53.4 mg/(m^2 · day). According to the local “wind rose”, this plot is under the influence of the main plume of emissions of the SCP (see Fig. 1, *a*) [4]. The electron microscopic study showed that aerosol particles consisted of three main groups: 1) particles of

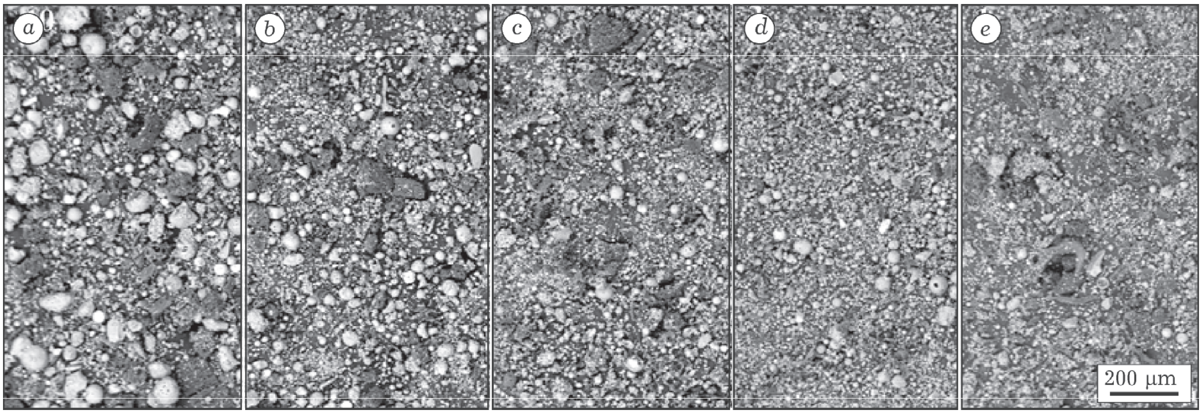

Fig. 2. Survey images of samples of aerosols in the regime of back scattered electrons. Sample number : 10 (*a*) 9 (*b*), 3 (*c*), 2 (*d*), 1 (*e*).

soot; 2) dominating group of aluminosilicate slags, mainly hollow spherical particles, often bubbly; 3) iron-containing spherical particles and their debris, including those in the close intergrowth with aluminosilicate slags. It should be noted that Fe-containing spheroids under an electronic microscope differ from the main darkened mass by the gray dim gleam; the content of iron in studied 75 individual particles varies from 8.18 to 95.85 mass % (with an admixture of Cu, Zn and other metals) (Table 1, Fig. 2).

Soot particles in aerosols

Within the limits of the major plume of emissions of the SCP, the content of soot in aerosols is low and equal to 15.4–17.9 mass % (see Fig. 1, *b*). However, at a distance of the first kilometres from settlements on the leeward side, increases dramatically and reaches 45.8 mass %. The contamination with soot of aerosols in the vicinity of the village of Sa-mus′ (points *5*, *6*) and in the suburbs of Seversk (point *10*) we associate with local emissions of local boiler houses and small enterprises. Soot particles, as a rule, have the tabular and irregular shape (see Fig. 2, points *9*, *10*). In aerosols near the villages of Naumovka and Georgiyevka large, elongated, swirling soot particles resembling the fibrous structure of the wood are meet (see Fig. 2, point *1*). Apparently, this form corresponds to the dominant local contamination from emissions of wood-burning heating. The surface of soot particles is cavernous, with a large number of cavities and pores, due to which small metal-containing particles adhere with ease to it. The spectrogram of 24 particles of soot shows that they on 80–100 % consist of amorphous carbon with impurities of O (up to 7–10 %), Si (up to 2–5 %), Al, S, K, Ca (0.*n* %).

Granulometric composition of aerosols

The granulometric composition of aerosols in the region changes naturally. In the nearest to Seversk sampling point (see Table 1, point *10*, in 6.85 km), aerosols are characterized by the abundance of large particles. Almost a third of the volume of aerosols is large aluminosilicate slag particles of the size of 50–150 μm, approximately 10 % – smaller aluminosilicate particles of the size 20–50 μm, predominantly of the spherical shape; approximately 20 vol. % – particles of soot of the size of 50–100 μm, mainly, in the form of tabular fragments; another 1–2 vol. % – iron-containing spheroids of the diameter of 20–40 μm (see Table 1, Fig. 2, point *10*). The rest (almost 40 %) – particles of the size smaller than 20 μm.

When removing on 13.2 km to the northeast from Seversk (point *9*), the proportion of large aluminosilicate spheroids and large soot particles decreases sharply (to 1 and 8 vol. %, respectively) (see Fig. 2). At the same time, the proportion of small aluminosilicate spheroids (20–50 μm) increases (up to 40 vol. %). The proportion of iron-containing spheroids of the diameter not exceeding 25 μm is approximately 1 vol. %.

At the distance of 21 km from Seversk (point *2*), the proportion of aluminosilicate spheroids of the size of higher than 20 μm in aerosols is decreased to 3.5 vol. % and the major mass (95 vol. %) is represented by particles of the size of less than 20 μm. At the distance of 27.8 km from Seversk, aerosol particles become even smaller (see Fig. 2, point *1*) with the exception of soot particles of the local origin that are characterized by a large size and elongated shape.

Therefore, as one moves aerosol emissions, in the atmosphere fractionating particles by their size, weight and particles shape occurs. Larger and denser particles fall out near the sources of pollution, and hollow fine aluminosilicate particles of the spherical shape, like and scaly and fine-graded particles migrate over long distances. At that, it is not excluded that heavy metal-containing microparticles may migrate over long distances in case of their attachment to hollow light balls and soot particles.

Microcomponent composition of aerosols

The microcomponent composition of the sol (mineral) part for all samples of aerosols is monotonous (mass %): SiO_2 64, Al_2O_3 21.7, Fe_2O_3 7.65 [4] (Table 2). Weak local variations of the composition of aerosols are observed near settlements: in the vicinity of the village of Samus’ and cities of Seversk and Tomsk they

TABLE 2

Integral macrocomponent composition of aerosols of the region of the Siberian Chemical Plant, according to the data of ICP-AES (excluding soot), mass %

Sample No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O	TiO_2	P_2O_5	SO_3	MnO
4	63.43	19.66	9.85	1.80	0.50	1.44	0.29	0.94	0.21	1.75	0.12
5	62.35	20.08	7.95	1.63	1.46	1.33	0.42	1.02	0.58	3.08	0.10
6	64.65	22.28	6.71	1.58	1.37	1.43	0.41	0.98	0.25	0.25	0.10
8	64.81	22.15	7.55	1.92	0.59	1.22	0.29	1.00	0.21	0.15	0.12
7	65.28	21.65	7.52	1.99	0.61	1.22	0.29	0.97	0.20	0.14	0.13
9	64.35	22.22	7.51	1.93	0.89	1.31	0.33	0.98	0.18	0.17	0.13
3	64.61	22.51	7.07	2.15	0.54	1.36	0.28	1.03	0.21	0.14	0.12
2	63.79	22.66	7.48	2.15	0.77	1.29	0.42	1.01	0.20	0.12	0.12
1	64.36	22.36	7.41	2.05	0.42	1.57	0.21	1.07	0.25	0.17	0.12
10	64.91	21.05	7.44	2.61	0.40	1.39	0.19	1.00	0.27	0.62	0.13
Average	64.25	21.66	7.65	1.98	0.75	1.36	0.31	1.00	0.26	0.66	0.12

are enriched with sulphur oxide SO_3 (up to 3 and 0.62 %, respectively). In our opinion, this is due to "the breath of the city" – emissions of small industrial enterprises, boiler-houses and transport [4]. In addition to sulphur, in aerosols of the neighbourhood of the village of Samus' a two-fold increase in the content of P (up to 1365 m. p.) at the average content of 660 m. p. is observed.

At a low technogenic dust-aerosol load to the north of the village of Samus' (points *5*, *6*), proportions of natural aerosols, including potassium-containing minerals are possibly increased. As a consequence, the proportion of K_2O in aerosols reaches here 1.46 % at its average grade of 0.75 %.

Phase composition of aerosols

Using the X-ray diffractometry major phases constituting the sol part of aerosols (in the descending order) were revealed: quartz, mullite and hematite.

In samples of aerosols taken near Seversk, the content of quartz is noticeably higher, in comparison with more remote sampling points: values of the peak intensity of quartz with $2\theta = 26.56°$ (where θ is angle of incidence of

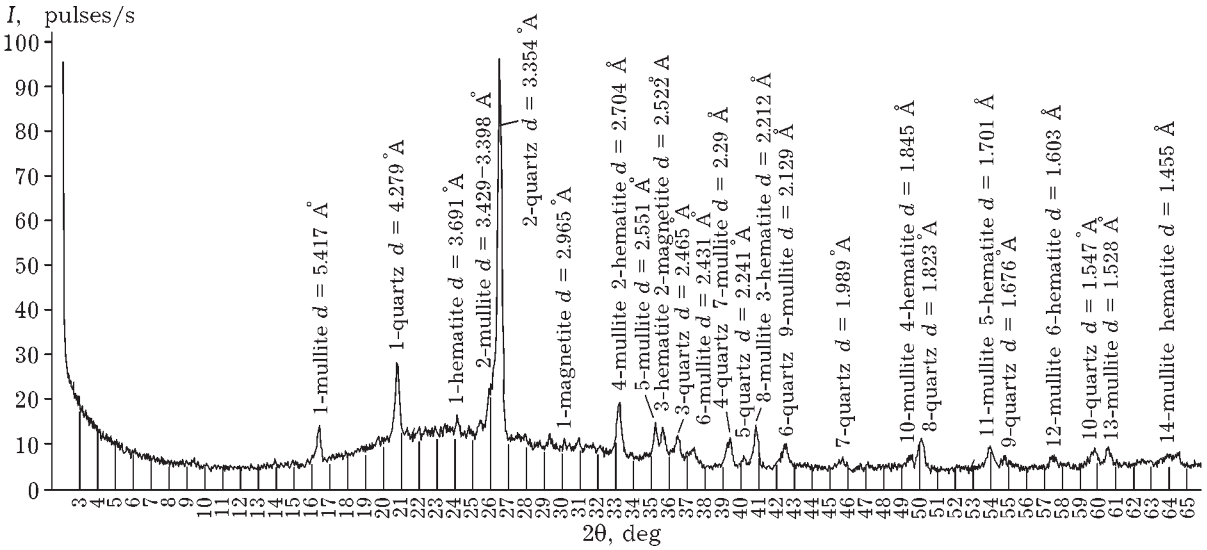

Fig. 3. X-ray diffractogram of aerosols of the sample No. 3 with the designation of the peaks of quartz, mullite, hematite and magnetite.

TABLE 3

Intensities of pulses of major mineral phases and X-ray amorphous gel on X-ray diffractograms of aerosols of the Siberian Chemical Plant, pulses/s

Points	Quartz								Mullite						Hematite*			Magnetite			XFA
	Peaks																				
	1	2	3	4	5	6	7	8	1	2	3	4	5	6	1	2	3	1	2	3	
2θ°	20.78	26.56	36.45	40.26	45.67	50.05	54.85	59.88	16.4	26	26.2	35.2	37	60.62	24.15	35.6	62.55	30.2	43.08	57	
d, Å	4.277	3.358	2.466	2.241	1.987	1.823	1.674	1.545	5.408	3.426	3.399	2.551	2.431	1.528	3.687	2.522	1.486	2.962	2.100	1.616	
4	20	92	7	2	2	8	3	5	8	12	19	8	2	5	3	6	2	0	0	0	12
5	17	80	5	3	2	7	2	4	8	10	16	7	2	5	0	5	2	0	0	0	12
6	18	83	5	2	3	6	2	5	7	8	15	6	3	3	0	5	0	1	0	0	12
8	18	92	6	3	3	9	4	5	9	12	21	9	3	5	4	8	2	2	0	1	13
7	16	74	5	2	3	7	1	3	9	12	19	8	3	4	3	7	2	2	0	0	12
9	18	94	6	3	3	8	2	5	8	12	18	9	3	5	3	8	0	0	0	0	12.5
3	17	86	6	3	3	7	3	4	8	12	18	9	3	4	4	7	0	3	0	0	12
2	18	79	6	2	2	8	3	6	8	13	20	9	2	5	3	8	3	1	0	0	12
1	13	67	5	3	1	6	0	3	8	10	18	7	3	4	3	6	2	0	0	0	12
10	24	100	7	3	4	12	3	7	7	11	17	9	3	6	4	6	2	1	0	0	11.5

* Peaks 2, 3 – hematite + magnetite.

the X-ray beam on the plane of the sample) and d = 3.358 Å (interplanar distance of the crystal lattice) in points *4*, *8*, *9*, *10* reach 92–100 pulses/s, and in point *1* only 67 pulses/s. (Table 3). Quartz is a dominating mineral phase and its proportion in aerosols accounts for approximately one-third.

Mullite of the variable composition from [$9Al_2O_3 \cdot 6SiO_2 \cdot (H_2O,\ F_2)$] to [$10Al_2O_3 \cdot 5SiO_2 \cdot (H_2O,\ F_2)$] – a typomorphic crystalline phase of technogenic aerosols that is formed when sintering fine-graded aluminosilicate particles at high temperatures. This mineral is not typical for natural aerosols of Siberia [5, 8]. All 14 peaks of mullite including four ones with parameters: 2θ = 16.37°, d = 5.417 Å; 2θ = 35.2°, d = 2.551 Å; 2θ = 37°, d = 2.431 Å; 2θ = 60.61°, d = 1.528 Å (see Fig. 3, Table 3) are clearly noticeable in X-ray diffractograms. This indicates a significant content of mullite in aerosols that – an average, 20 %.

Aerosols of the region are enriched with silica (see Table 2), about a half of which (33 from 64 %) is represented in the form of quartz crystals. For mullite, the ratio of Al_2O_3/SiO_2 = (70–76) : (22–28)) *i. e.* silica amounts to about one third. Consequently, the proportion of silica bound with mullite reaches almost 7 %. Thus, by the roughest estimates, out of 64 % of the total content of silica in aerosols approximately 40 % falls on the quartz and mullite. Where else in aerosols can 24 % of free silica be concentrated?

Judging by a high X-ray amorphous halo, in diffractograms in technogenic aerosols, the content of the X-ray amorphous phase is significant, which agrees with the data of other researchers [5, 8]. The X-ray amorphous phase consists of glass particles and crystals, the sizes of which do not exceed the wavelength of the copper X-ray radiation CuK_α, equal to 1.54178 Å. In aerosols of the study region, the proportion of the X-ray amorphous phase is assessed approximately in 25 %. Most likely, free silica is concentrated precisely in this phase.

Using a scanning electronic microscope 68 particles of aluminosilicate spheroids with the size of 8–50 μm were studied (Table 4). Despite a broad diapason of variations, the particles composition is monotonous for all sampling points and, as expected, close to the average composition of aerosols (see Tables 2, 4, Fig. 4, *a*),

TABLE 4

Macrocomponent composition of individual aerosol aluminosilicate slag particles-spheroids in the area of Siberian Chemical Plant, according to data of an energy dispersive spectrometer (EDS) OXFORD built in into a scanning electronic microscope LEO 1430 VP, mass %

Samples*	R**, km	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O
4 (7)	16.3	59.1	27.4	4.53	0.91	2.69	0.58	1.39	3.40
5 (2)	22.8	55.6	28.4	8.2	1.23	1.14	0.93	1.80	2.74
8 (2)	14.8	70.2	19.2	2.4	<0.4	<0.4	1.65	3.80	2.69
9 (11)	13.2	61.9	24.7	4.55	0.22	2.34	3.04	0.46	2.83
3 (21)	16.9	61.2	29.0	3.06	1.11	1.31	0.68	1.32	2.29
2 (2)	21.0	64.7	26.0	1.1	0.85	0.32	0.48	3.67	2.85
1 (8)	27.8	71.0	19.6	3.18	0.16	0.76	1.34	0.95	3.00
10 (15)	6.85	62.3	25.6	3.76	0.73	0.99	1.4	1.9	3.29
Average (68)		62.7	25.9	3.69	0.71	1.41	1.32	1.43	2.84
Maximal		85.6	42.3	19.7	7.01	18.17	9.48	8.38	7.38
Minimal		40.8	9.28	0.48	<0.4	<0.4	<0.4	<0.5	0.39

* A number of particles-spheroids is given in brackets.

** Distance from town Seversk.

except for the content of Fe, Na, and K. The studied aluminosilicate spheroids contain four times more the alkaline bases Na_2O and K_2O, in comparison with the average integral composition of aerosols. The content of iron in them, on the contrary, is two times less, in comparison with the average integral composition, in which Fe-containing spheroids contribute.

If one assumes that the entire contained alumina Al_2O_3 (in average 25.9 mass %) in aluminosilicate spheroids is spent on the formation of mullite, then 8–10 % of SiO_2 is required for the same amount of Al_2O_3. Consequently, aluminosilicate spheroids approximately on 35.9 % consist of mullite. Since aluminosilicate spheroids on average on 62.7 % consist of SiO_2, then after deducting the amount of silica bound with mullites, 52.7 % of SiO_2 remains free and is supposedly present in the form of quartz and silica glass. If one assumes that in our sample of aluminosilicate spheroids, quartz and the X-ray amorphous phase are in the same ratios, as in general in aerosols, then the proportion of each of these phases is approximately 25 mass %. Therefore, aluminosilicate spheroids

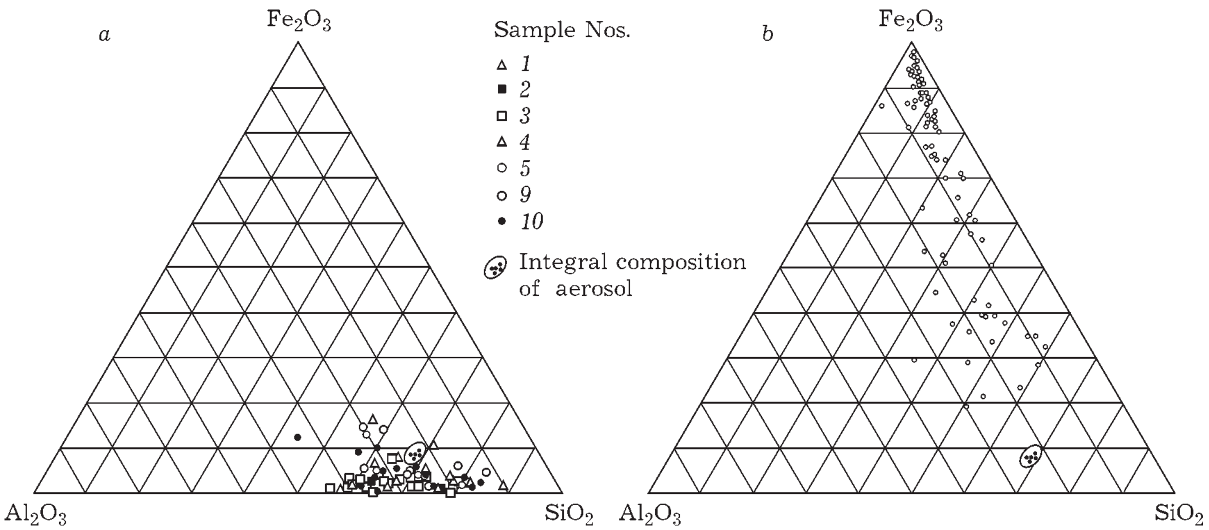

Fig. 4. Content of SiO_2, Al_2O_3, Fe_3O_3 (in mass %) in aluminosilicate spheroids (*a*) and iron-containing spheroids (*b*) of technogenic aerosol of the district of Seversk.

are apparently composed of quartz, mullite and glass (SiO_2 with impurities of Fe, Ca, Mg, K, Na and other elements) (Table 5).

The peak of hematite $2\theta = 24.15°$, $d = 3.691$ Å with the intensity up to 4 pulse/s, is well expressed in the diffractograms (see Table 3, Fig. 3). In the diffractograms of aerosols for the points *2*, *3*, *6–8*, and *10*, a very weak peak of magnetite $2\theta = 30.19°$, $d = 2.965$ Å with the intensity of no more than 2 pulses/s is discovered. The second peak with $2\theta = 43.08°$, $d = 2.10$ Å is absent at all, and the third peak with $2\theta = 57.0°$, $d = 1.616$ Å with the intensity of 1 pulse/s can be difficult to highlight on the single diffractogram (point *8*). Therefore, the basic Fe-containing mineral in aerosols is hematite, and not magnetite and magnesioferrite, as was previously thought [5]. The composition of Fe-containing spheroids varies from alloys of aluminosilicates with hematite and magnesioferrite to fully hematite and magnesioferrite (see Fig. 4, *b*). When increasing the content of Fe on the surface of aluminosilicate spheroids (Fig. 5, *a*) hematite crystallizes in the form of dendrites (*b*), polygonal crystals (*c*) and their intergrowths (*d*). The trigonal syngony of hematite crystals is clearly recorded in images. Iron-containing crystals of the cubic syngony, presumably of magnetite (see Fig. 4, *e*) are observed on the surface of aluminosilicate spheroids in isolated cases. Magnesioferrite, as a rule, forms spheroids with original, symmetrical, skeletal structure of the surface (see Fig. 5, *f*, *g*). In the form of small spheroids, particles of native iron with the content of Fe of about 96 % that contain impurities of Mn (up to 9.9 %), Zn (up to 9.2 %), K (up to 2.2 %), Sn (up to 1.7 %), Ti (up to 1.18 %) are found. Iron containing spheroids as aluminosilicate are hollow inside (see Fig. 5, *h*).

Usually, the proportion of calcium in iron containing spheroids is insignificant, *viz.*, from 0.7 to 1.39 %. Exceptions are two subgroups of spheroids where the content of Ca is higher. Spheroids of the first subgroup have the “corroded” cavernous surface (see Fig. 5, *j*) and contain up to 25 % of calcium (an average of 20 %). The second subgroup is spheroids, the surface of which is characterized by the “intricacy” (see Fig. 5, *k*). They contain 2–3 % of calcium. Rare shapeless slag masses of CaO are found in aerosols of the main plume of emissions of the SCP, which agrees with results of the X-ray diffraction.

According to data of the X-ray diffraction, the content of hematite in aerosols of the main plume of emissions of the SCP is approximately 10 % and it is reduced by almost half in the periphery.

Among Fe-containing particles, in addition to spheroids, rare angular, splintery, twisted

TABLE 5

Mineral phase composition of aerosol aluminosilicate slag particles-spheroids in the region of the Siberian Chemical Plant, %

Samples*	*R***, km	Glass (SiO_2 with admixtures of Al, Fe *etc.*)	Mullite ([$9Al_2O_3 \cdot 6SiO_2 \cdot (H_2O, F_2)$])	Quartz (SiO_2)
4 (7)	16.3	~25	36–38	23–26
5 (2)	22.8	~25	37–40	19–22
8 (2)	14.8	~25	25–27	38–40
9 (11)	13.2	~25	32–34	27–30
3 (21)	16.9	~25	38–40	25–28
2 (2)	21.0	~25	34–36	30–32
1 (8)	27.8	~25	25–27	38–40
10 (15)	6.85	~25	33–36	27–30
Average (68)		~25	34–36	34–37
Maximal		~25	55–59	41–46
Minimal		~25	12–13	33–35

* Number of particles in particles-spheroids is given in brackets.

** Distance from Seversk.

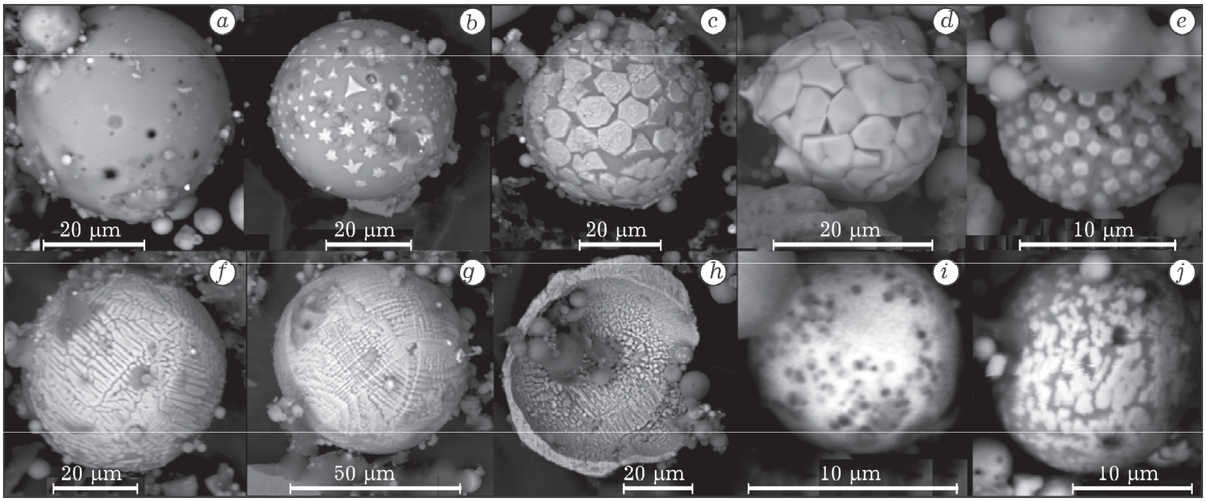

Fig. 5. SEM images in the mode of back-scattered electrons: crystallization of hematite on the surface of aluminosilicate hollow spheroids (*a*–*d*); crystallization of magnetites on the surface of aerosol spheroid (*e*); aerosol magnesioferrite spheroids (*f*–*h*); cavernous (*i*) and "patterned" (*j*) surfaces of iron-containing spheroids enriched with calcium.

formations with impurities of Cr, Mn, Ni, Zn, C and O are found, the content of which varies from 0 to 50 %. Supposedly, this is particles of chrome steel, cast iron and other iron alloys oxidized to varying degrees. Crystals of natural pyrite, of chalcopyrite and their debris are very rarely observed in aerosols. The following minerals (in descending order) are also registered: plagioclases, potassium feldspar, calcite, ankerite, anhydrite, mica, siderite, amphiboles. Apparently, among quartz particles mainly of the anthropogenic origin natural quartz, fragments of crystals of which were rarely registered under the electronic microscope is also present.

Total 238 particles that contain elements with a relative atomic mass of more than 56 (heavier than Fe) has been found on the surface of a thin layer of aerosols with the total area of 470 mm^2. Their size on average does not exceed 10 μm. From them, 98 particles are compounds of lithophile and rare earth elements, *viz*., geochemical indicators of emissions of the SCP [4]:

1. 45 particles are oxides and phosphates Y, lanthanoids (La, Ce, Nd, Sm, Gd, Dy, Er), radioactive TH and elements of the platinum group (Os, Ir). Some particles on the composition are close to the monazite. Herewith, within the main loop of the SCP emissions they occur 2–3 times more often than in the periphery. Typically, the particle size does not exceed 5 μm, they are affixed to the surface of larger particles and surrounded by alumosilicates mass.

2. 36 particles are Ba phosphates and sulphates with the impurity of Sr. The smallest particles including those in the form of spheroids with the size of up to 5, rarely to 10–20 μm (Fig. 6, *a*).

3. 17 particles are silicates with Zr, as a rule, in the form of small elongated crystals, possibly of zirconium (see Fig. 6, *b*). Zr and REE are occasionally included in aluminosilicate slags (see Fig. 5, *c*, *d*). This composition of slags indicates high temperatures of their formation. Compositions of aluminosilicate slags with Zr and REE, as well as phosphate spheroid Sr–Ba are presented in Table 6. It should be noted that in aerosols particles of U oxides (with the content of 1–2 %) are absent. Consequently, uranium that is of the major geochemical indicators of the SCP is present in aerosols in the diffuse form.

Among particles of chalcophile and lithophile elements, the following are found most often: Sn oxides (25 particles), close to cassiterite in the structure; the wreckage of W (19 particles); Sb oxides in the form of octahedral crystals (14 particles). Tungsten particles are distinguished by very small sizes (0.*n*–2 μm). Chalcophile particles of Sb, Pb, Mo and lithophile of Sn form independent mineral allocations mainly in the form of oxides, more rarely car-

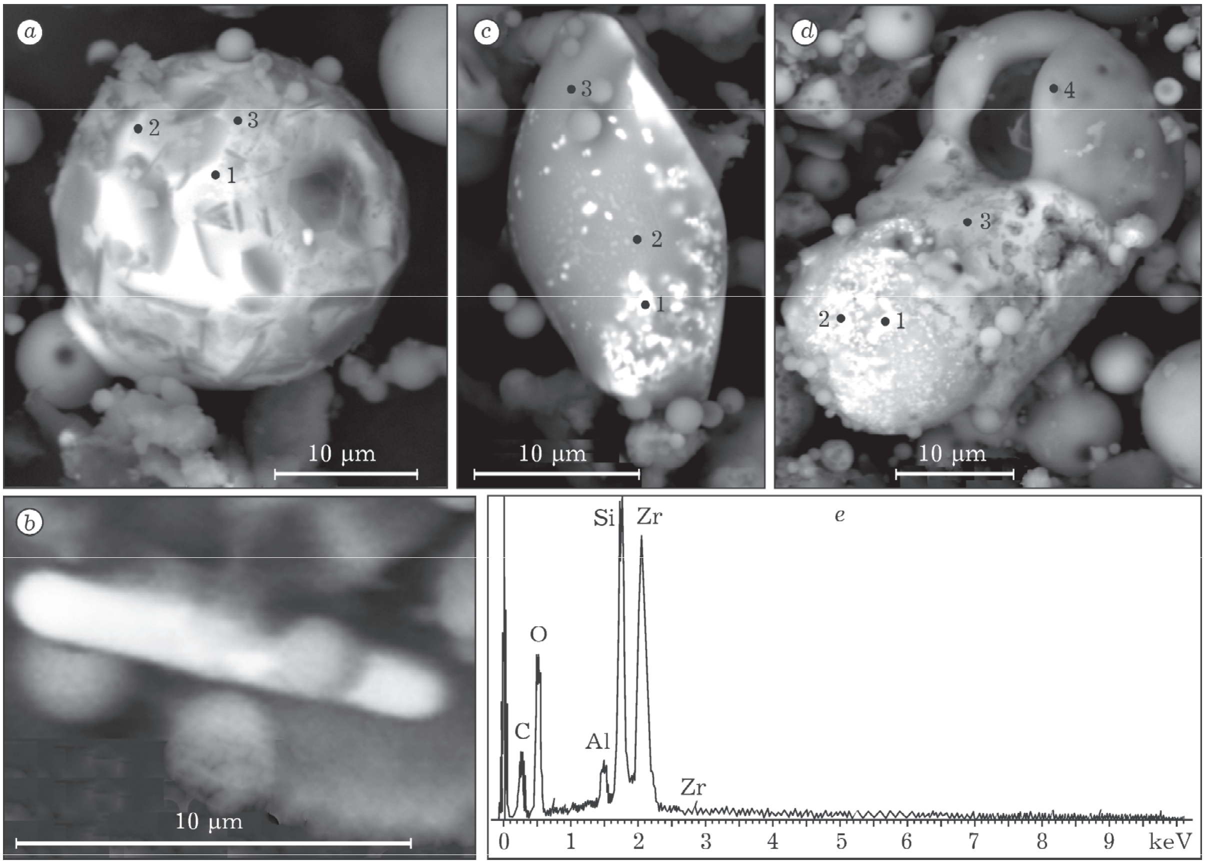

Fig. 6. SEM images of aerosol particles-indicators of emission of the Siberian Chemical Plant in the mode of back-scattered electrons. The location of points of spectrometric scanning: *a* – spheroid of Ba and Sr phosphates, *b* – crystal of $ZrSiO_4$, *c* – the alumosilicate slag particle with an admixture of $Fe(Mn)_2O_3$ and $ZrSiO_4$, *d* – aluminosilicate slag particle with REE phosphates, *e* – the spectrum of the crystal of $ZrSiO_4$.

TABLE 6

Elemental compositions of particles in scanning points, mass %

Point No.	O	Al	Si	P	Fe	S	La	Ce	Nd	Zn	Na	Mg	K	Ca	Ti	Sr	Ba	Mn	Zr
*Slag spheroid with Ba-Sr phosphates (*see Fig. 6, *a)*																			
1	38.76	14.68	0.53	12.06	1.82	0.93	–	–	–	–	–	–	–	–	–	5.15	26.09	–	–
2	51.35	22.07	1.68	7.63	–	–	–	–	–	–	–	–	–	–	–	3.45	13.82	–	–
3	43.58	15.39	1.44	10.73	–	–	–	–	–	–	–	–	–	0.19	–	4.8	23.87	–	–
*Aluminosilicate slag particle with Zr (*see Fig. 6, *c)*																			
	O	Al	Si	–	Fe							Mg	K	Ca	Ti	–		Mn	Zr
1	40.6	4.33	7.78	–	8.14	–	–	–	–	–	–	–	1.12	0.24	–	–	–	–	37.79
2	45.69	10.28	20.53	–	14.6	–	–	–	–	–	–	0.27	2.72	0.47	0.27	–	–	0.33	4.83
3	59.77	9.38	17.16	–	8.18	–	–	–	–	–	–	0.42	1.86	0.47	0.3	–	–	–	2.46
*Aluminosilicate slag particle with REE phosphates (*see Fig. 6, *d)*																			
	O	Al	Si	P	Fe	S	La	Ce	Nd	Zn	Na	Mg	K	Ca	Ti	Sr	Ba	Mn	Zr
1	41.7	6.9	12.7	8.5	–	–	6.93	13.6	4.28	3.2	–	0.9	0.7	0.64	–	–	–	–	–
2	48.0	8.1	12.3	6.3	1.1	–	4.94	10.8	3.72	3.2	–	–	0.96	0.64	–	–	–	–	–
3	56.2	2.9	16.7	–	5.9	0.7	–	–	–	–	–	–	–	15.4	2.28	–	–	–	–
4	57.3	7.4	30.4	–	0.9	–	–	–	–	–	1.5	0.68	1.84	–	–	–	–	–	–

Note. The dash – below the detection limit.

bonates, the silicites and silicates, their sizes can reach 10 μm and higher. Pd phosphates and Bi oxides have been registered. Often, metals Zn, Co, Ni are present in the form of impurities (>2 %) in Fe oxides. Natural galena (single particles) has been discovered.

The chalcophile geochemical specifics of the local aerosol pollution near the settlement of Samus' [4] is manifested in the mineral composition of aerosols: Cu, Zn, Fe sulphides in the form of fragments of pyrite, chalcopyrite and sphalerite (seven particles were studied), Mo oxides adhering to the soot particles (ten particles were studied). These sulphide particles are apparently related to low local emissions.

A number of elements with a negligible gross content form independent mineral allocations, such as, for example, sulphides of silver with admixtures of with Ga (8 particles in the sample of point *10*) and five aerosol particles of "native" Au.

CONCLUSION

It has been established that technogenic aluminosilicate and Fe-containing slag spheroids and soot particles dominate in aerosols at a low content of natural minerals. As one moves aerosol emissions in the atmosphere larger and more dense particles fall near sources, and hollow-centred fine aluminosilicate particles of the spherical shape, scaly and finely-dispersed particles, as well as heavy metal-containing particles, adhered to them, migrate at long distances. In case if heavy particles are attached to light "floating" particles, distance of their mass transfer significantly increases.

Using X-ray diffractometry it has been established that aerosols are mainly formed by quartz, X-ray amorphous phase, mullite and hematite (in the descending order). Among Fe-containing phases, hematite dominates magnetite and magnesioferrites. The study of aluminosilicate and Fe-containing spheroids under the electronic microscope with the built-in microscope has shown that the macrocomponent composition of dominating groups of aerosols (excluding soot) is monotonous and it is mainly shaped from three components (%): SiO_2 64, Al_2O_3 21.7, Fe_2O_3 7.65. Using the atomic-emission and mass spectrometric analysis on the inductively coupled plasma it has been established that the same Si, Al, Fe [4] prevail in the composition of aerosols. Under the conditions of the oxygen environment and high temperature conditions of the formation of aluminosilicate slags the most probable form of finding aerosol forming elements of Si, Al, Fe are undoubtedly oxides. The calculated oxide composition virtually matches the average composition of aluminosilicate spheroids that are a dominating group of aerosol particles. Mullite, quartz and silica glass are probably basic phases folding aluminosilicate spheroids. When increasing the content of Fe a gradual transition of aluminosilicate spheroids into Fe-containing is observed.

Based on the analysis of the distribution and composition of aerosol particles including particles with heavy elements high and low temperature types of technogenic aerosols that are related to three main sources of emissions on the area of Seversk have been selected.

1. The low-temperature type of the local scale. Aerosols formed by sources of the local scale., *viz.*, emissions of wood and coal heating small boilers and companies of the villages of Naumovka, Georgiyevka and the settlement of Samus' [4] is characterized by a high content of soot, the presence of sulphides of chalcophile elements Pb, Zn, Cu and Sb, Mo oxides (apparently, impurities in coal) in their composition.

2. The low-temperature type. In aerosols of so called the breath of the city of the long scale generated by integral emissions of numerous small enterprises and transport of both Seversk and neighbouring Tomsk, typomorphic phases are splinters of steal (almost 100 % from Fe), cast iron (Fe with the content of C), complex oxides of tungsten and tin, particles of silver sulphides, as well as gold particles. Gold microparticles, as a rule, are attached to larger soot particles.

3. The high-temperature type of the regional scale. In aerosols generated by emissions of SCP of the regional scale sooty particles are contained in small amounts. topomorphy phases are aluminosilicate are presented by aluminosilicate hollow spheroids that contain from mullite, quartz and glass SiO_2. When increasing the content of Fe in slugs hematite (1–2 % of the total mass of aerosols), magnetite and magnesioferrite are crystallized. Geochemically, indi-

cators of emissions of SCP in the form of REE, Y, Th, Sr, Ba in aerosols are present in the form of oxides, phosphates, including zirconium silicates and REE phosphates, rarely, Ba, Sr sulphates.

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