

Colloidal Component of Granulodensimetric Soil Fractions

G. N. Fedotov^a and Z. S. Artem'eva^b

^a Institute of Ecological Soil Science, Moscow State University, Vorob'evy gory, Moscow, 119992 Russia
e-mail: gennadiy.fedotov@gmail.com

^b Russian State Agricultural University—Moscow Agricultural Academy, Russian Academy of Sciences,
ul. Timiryazeva 49, Moscow, 127550 Russia

Received October 18, 2012

Abstract—Granulodensimetric soil fractions isolated from chernozem, gray forest soil, and soddy-podzolic soil have been studied using a scanning electron microscope. The studies confirmed that the light fractions with density $<1.8 \text{ g/cm}^3$ and particle size $>53 \text{ }\mu\text{m}$ mainly consists of plant residues; however, they also contain mineral particles covered with relatively thick organomineral films and carbonaceous substances. It has been shown that the clay fraction consists of a mixture of ultramicroaggregates of clay minerals $\leq 1 \text{ }\mu\text{m}$ in size covered with a hydrophilic organomineral gel, and the organic matter of the residual fraction includes a stable highly aromatized (lignin-like) material, as well as coals and coal-like materials.

Keywords: scanning electron microscopy of soils, fractal clusters of humic substances, study of granulodensimetric soil fractions

DOI: 10.1134/S1064229315010044

INTRODUCTION

Numerous works relating the properties of soils and their degradation with the content of labile (easily decomposable) organic matter (LOM) have been published in the past decades [4, 5, 8]. Different methods have been proposed for the isolation of this fraction of soil organic matter (OM) [4, 5, 8–10], which relatively adequately reflect the revealed correlation for different soils.

To specify the concepts of soil OM, some authors [1–3, 6, 11–15] studied organomineral compounds in more detail and isolated them by granulodensimetric fractionation.

This method separates the soil sample into the light fractions (LFs), the residue, and the clay fraction.

Let us dwell on the current concepts of the LFs isolated by this method [2]:

(1) It is believed that the fragments of plant origin prevail in the fraction $<1.8 \text{ g/cm}^3$ with a particle size of $>53 \text{ }\mu\text{m}$.

(2) It is believed that the OM in the silty-sized fractions (density $<1.8 \text{ g/cm}^3$, particle size $<53 \text{ }\mu\text{m}$) contains microbiologically transformed plant material and mainly consists of humic substances, some products of incomplete humification of organic residues, and carbonaceous particles.

(3) No isolated plant fragments were found in the fraction of $1.8\text{--}2.0 \text{ g/cm}^3$. It is believed that the OM included into biophytoliths prevails in this fraction, and the fraction is referred to as the phytolith fraction.

It was also shown that the content of OM decreases in both the LFs and clay during the degradation of soils, but the rate of this decrease in the LFs is significantly higher [1, 2, 11, 14]. As a result, the content of C_{org} in the LFs, the portion of C_{LF} in the total carbon accumulation in the soil (C_{tot}), and the ratio between the contents of C_{org} in the LFs and the clay ($C_{\text{LF}}/C_{\text{cl}}$) were proposed to be considered as indicators of the OM status in the soil.

It should be noted that the concepts of the fractions isolated by this method were based on their study using predominantly methods of chemical analysis and optical spectroscopy. The authors considered the soil as an organomineral system and supposed that pedogenesis processes mainly result in the formation of organomineral-interaction products, which can be isolated in the weakly transformed state by the method of granulodensimetric fractionation, and the nature and properties of their solid phase can then be studied. However, insufficient attention was given to the role of the consolidating components or, more exactly, the organomineral colloidal compounds (gels) that cover and bind the soil particles.

The concepts of the structural organization of soils have changed by now. It follows from the colloidal-chemical model of soils [17] that organomineral gels mainly composed by fractal clusters of humic supramolecules (F clusters) [16] cover and bind the soil particles, which transforms the soil into a unified system. The supramolecules of humic substances and the F clusters have different hydrophilic–hydrophobic properties, which can strongly vary, as well as the

thickness of the gel layers combining the soil particles in different points of the soil sample.

This system cannot be completely separated into particles with different specific weights in liquids of different densities, because the soil gels cannot be completely disintegrated by physical and physico-chemical methods. These methods separate not particles but their agglomerates having particular densities, into which the soil sample can be disintegrated under the effect of specific mechanical impacts capable of destroying the binding gel layer and detaching the agglomerates with lower density than the liquid used.

It should also be noted that the granulodensimetric fractionation is not only the separation of the particles by their density. The presence of numerous voids in dry soil structures and the possibility or impossibility of their filling with liquids significantly affect the result; hence, the degree of surface wetting of the soil particles (or, more exactly, organomineral gels occurring on their surfaces) by the liquids used for fractionation is of great importance in these processes.

All the aforesaid points to the complexity and ambiguousness of the granulodensimetric fractionation of soils and the necessity for extending our knowledge concerning this issue.

The aim of this work was to specify the role of the colloidal soil component in granulodensimetric fractionation by studying isolated soil fractions using electron microscopy, microanalysis, and chemical analysis.

It should be noted that no data on the direct observation of F clusters in the soil samples by scanning electron microscopy are available by now. Therefore, the existence and observability of F clusters in soil samples should be confirmed at the first stage of work for the correct interpretation of the scanning electron microscopy data for different granulodensimetric fractions.

OBJECTS AND METHODS

To solve the first problem, zonal soil samples from the collection of the Faculty of Soil Science of Moscow State University were used: an iron-illuvial podzol, a podzolic soil, a soddy-podzolic soil, a gray forest soil, different chernozem types, light and dark chestnut soils, a brown semidesert soil, a sierozem, a krasnozem, and peat soil, as well as samples taken from the humus-accumulative horizons of a soddy-podzolic soil near the Yakhroma River floodplain and a typical Kursk chernozem.

The objects of studying the fractions isolated by the granulodensimetric method from the soddy-podzolic soils of the southern-taiga subzone were soddy-podzolic soils from Moscow oblast, which cover the main combinations of particle-size and lithological diversities. The upper A1 horizons of forest soils were studied: a sandy loamy soddy-strongly podzolic soil on shallow light loam underlain by glaciofluvial sands (Zvenigorod

biostation), a sandy loamy soddy-strongly podzolic soil on heavy cover loam (Chashnikovo Educational-Experimental Soil-Ecological Center), a loamy weakly soddy-medium-podzolic soil on morainic loam (Malinki Station of the Severtsov Institute of Ecology and Evolution), and a loamy soddy-podzolic soils on binary cover loams underlain by glaciofluvial deposits (Zelenograd Station of the Dokuchaev Soil Science Institute). In the zone of gray forest soils, a heavy loamy gray forest soil with a second humus horizon on a thick loess-like loam (Ivan'kovo Station of the Dokuchaev Soil Science Institute) was studied. In the chernozem zone, the upper A1 horizons of virgin soils—undeveloped, typical, and leached chernozems from the Privolzhszkaya Lesostep Reserve—were studied.

The soil OM was studied using the modified version [14] of the granulodensimetric method developed earlier [20]. The LFs were isolated by a simplified procedure using a bromoform-ethanol mixture with densities of 2.0 and 1.8 g/cm³ after the ultrasonic treatment of the soil suspension for 15 min (180–200 W, 22 kHz) to remove the clay. The fractions with density <1.8 g/cm³ were separated using a 53- μ m sieve into two subgroups: the free (not aggregated) particles >53 μ m in size and the aggregated particles <53 μ m in size. It was earlier shown that the isolation of free OM (LF_{free}) after the removal of the clay fraction has no significant effect on the amount and qualitative composition of the LF_{free} isolated by the complete procedure (before the removal of the clay fraction) [14].

The carbon was determined by wet combustion according to the Tyurin method version used in the Laboratory of Soil Biochemistry of the Dokuchaev Soil Science Institute. The nitrogen was determined by the Shaimukhametov version of the Kjeldahl micromethod [19].

The electron microscopic studies were performed using a JEOL-6060A scanning electron microscope (Japan) with a tungsten cathode. The microanalysis was performed using a JEOL EX-2300 BU energy-dispersive X-ray spectrometer.

The scanning electron microscopy data are characterized by the variation of the image intensity depending on the heights of the different parts of the target. The instrument is adjusted so that the highest details in the field are light gray, and the lowest ones are dark gray. Hence, the minimum perceptible height difference depends on the maximum height difference in the studied area. Therefore, if the height difference in the studied region of the soil sample is around several microns, the adjacent and contacting F clusters cannot be distinguished, because the height difference between the upper part of the clusters and the inter-cluster zone does not exceed a few tens or even several nanometers. This does not allow acquiring high-quality information at the study of soils and requires the isolation of their particles and the application of them on a smooth (preferably atomically smooth) surface.

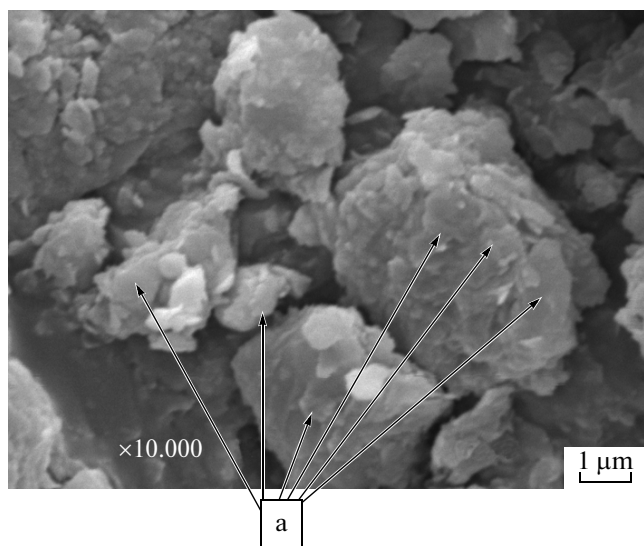


Fig. 1. Electron microscopic image of soil gels in the OA horizon of a podzolic soil: (a) platy formations.

It should be noted that the representativeness of the studied portion is the main problem faced at the preparation of samples for electron microscopic study. However, the soil particles differ in their properties and binding strength; therefore, the preparation procedure must ensure the absence of segregation by the properties and binding energy to the soil sample.

Therefore, a new, dry method was used at the preparation of the samples for revealing F clusters on the surface of soil particles. Soil particles were applied onto the atomically smooth surface of freshly split mica by mechanical contact with air-dry soil. The soil sample was preliminarily shaken in a glass vial till the degradation of the soil aggregates. The excess soil was removed from the mica by an air stream. This method allowed avoiding the selective application of particles, because the mechanical impact on the soil under shaking separated any particles from the soil aggregates without their differentiation by properties and binding strength to the soil material. At the preparation of the samples by the application of particles onto the atomically smooth mica surface by this method, the height difference in the studied area was minimized by selecting smooth surfaces of mineral particles parallel to the support surface.

RESULTS AND DISCUSSION

Study of air-dry soil samples. It was noted at the study of these samples that the surface of the soil particles and their aggregates more than several microns in size is most frequently roofed with platy formations (a) apparently from layered minerals (Fig. 1).

These platy formations, as well as fine particles of other shapes, were isolated from the soil by the dry method, applied onto the surface of mica, and thor-

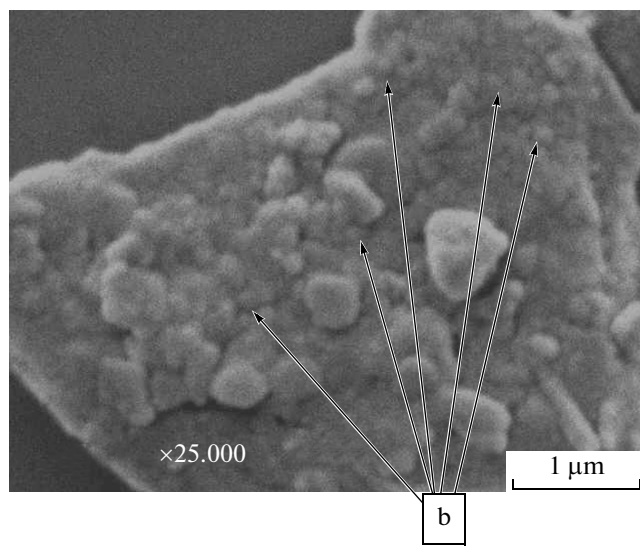


Fig. 2. Electron microscopic image of a soddy-podzolic soil particle on mica: (b) F clusters of humic substances.

oughly studied. It was found that all the soil particles on the support were covered with clusters (b) 100–200 nm in size (Fig. 2). The method used for the separation of the particles showed that the surface of the soil particles is completely covered with these clusters.

However, these clusters could be either F clusters or some mineral structures of iron, aluminum, silica, etc. The study of their morphology gave no unambiguous answer to this question.

To rectify our concepts concerning these clusters, a microanalysis was performed for numerous particles of different shapes and sizes isolated from a soddy-podzolic soil and applied onto the surface of atomically smooth mica. The size of the zone emitting the characteristic X-ray photons exceeds the thickness of the film formed by clusters on the surface of the particles and, in some cases, even the thickness of the layered material on which these clusters are fixed; therefore, the characteristic radiation bears information about the compositions of the clusters, the thin layered minerals, and the mica support. The atoms of the elements entering in the clusters should produce emission in all cases, but the atoms of the mineral particles on which they are located and especially of the mica support emit only if the thickness of the films formed by the clusters or the total thickness of these films and mineral particles is lower than 1–2 μm. In fact, this is proved by a contradiction: if an element is beyond the clusters, it will be not observed at the study of all the mineral particles. Only the elements forming the clusters or those entering in the mineral particles on which the thin films of clusters occur should always be observed.

The microanalysis of different mineral particles isolated from the soils revealed only silicon and carbon in all the cases. The result is sufficiently logical,

because silicon enters in the composition of the most abundant soil minerals (quartz, feldspar, layered aluminosilicates) and carbon is in F clusters. However, the obtained data also suggest that the surface of the minerals is covered with clusters of two kinds: F clusters and silica clusters.

To rectify our concepts of these clusters forming the basis of soil gels, the OM was removed from the soil sample by its oxidation in a water environment with an acid solution of potassium dichromate followed by the study of the soil particles by scanning electron microscopy. The study of the microphotos revealed that the clusters that had been observed before the removal of the OM almost completely disappeared from the surface of the particles. This suggests that either some silica formations of similar morphology are present among the F clusters covering the surface of the soil particles or we observe residual OM, which always remains in the sample after oxidation, in the form of F clusters.

The performed experiments unambiguously indicated that the surface of the soil particles is covered with a layer of F clusters. This allowed the conclusion to be drawn that the soil aggregates are formed due to the interaction between the mineral particles covered with F clusters, i.e., that the contact between the mineral particles in the soil aggregates is mainly performed via F clusters.

The study of the LF_{free} fraction under an electron microscope revealed that, along with the well distinguished fragments of plant material at different degrees of decomposition (Fig. 3), complex particles of various shapes (rounded, rectangular, irregular) are found in a large amount in the fraction. They can be identified as particles of primary minerals (feldspar, quartz) covered with organomineral formations from layered minerals and the layer of F clusters on their surface. It should be noted that the virgin chernozem contains significantly larger amounts of these formations (up to two-thirds of the total number of particles) than in the soddy-podzolic soil, which is mainly composed of residual plant material.

The microanalysis data (Table 1) confirm the suppositions based on the morphology of the particles observed in the microphotos: the content of carbon is 75 mol % for the mineral particles covered with organomineral gels and up to 90 mol % for plant residues and carbonaceous substances. It should be noted that the energy-dispersive detector used for light elements gives only qualitative indications of their content; hence, we cannot confidently discriminate plant residues from carbonaceous substances.

The obtained data allow concluding that, first, the organomineral gels covering the mineral particles are enriched with humic substances, which ensure the impermeability of the gel films and decrease the total density of these formations. This is most manifested in chernozems. Second, it is confirmed that the plant residues in the soils of forest cenoses contain significantly larger amounts of woody species than those in

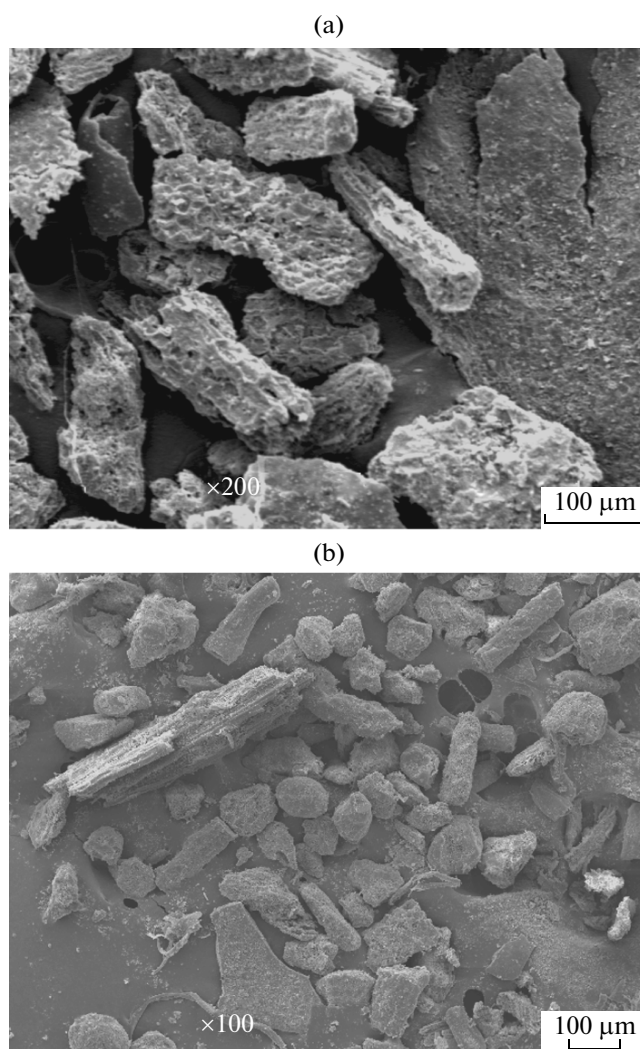


Fig. 3. Images of the light fractions of aggregated OM with density $<1.8 \text{ g/cm}^3$ and particle size $>50 \text{ }\mu\text{m}$ isolated from (a) forest soddy-podzolic soil and (b) chernozem.

the chernozems, where herbaceous plants are absolutely dominant. This affects the rate and degree of their mineralization, which are higher in the chernozems. The presence of hardly decomposable components, including lignin, in the woody residues (up to 25–30% compared to 15–20% in herbaceous plants), in combination with the less favorable climatic conditions for microbiological activity in the forest soils than in the chernozems (high moisture content and low temperatures), determines their lower degree of decomposition and the accumulation of plant residues in this fraction.

The visual appearance of the aggregated LF with a density of $<1.8 \text{ g/cm}^3$ and a particle size of $<53 \text{ }\mu\text{m}$ (LF_{agr-1}) strongly differs from that of the LF_{free} . The fraction is a relatively homogeneous powdered material black in color.

Table 1. Contents of elements in the light fractions isolated from soils by granulodensimetric fractionation

Soil	Fraction	Experiment no.	Elements, mol %							
			C	Si	Al	Fe	Mg	K	Na	Ca
Soddy-podzolic soil	1.8–2.0 g/cm ³	1	61.6	25.7	7	2.5	1.8	1.4	–	–
		2	62.1	25.8	5.9	2.9	1.6	1	0.7	–
		3	67.4	28.7	1.8	2.1	–	–	–	–
	<1.8 g/cm ³ , <53 μm	1	72	20.3	2	3	–	1	–	1.7
		2	94.4	2.2	0.9	1.7	0.8	–	–	–
		3	62	37.2	0.8	–	–	–	–	–
	<1.8 g/cm ³ , >53 μm	1	91.6	2.8	3.2	2.4	–	–	–	–
		2	90	6.3	2	1.3	–	0.4	–	–
		3	93.1	2.1	2.4	2.4	–	–	–	–
Gray forest soil	1.8–2.0 g/cm ³	1	52.7	46.6	0.7	–	–	–	–	–
		2	76.6	17.2	2.9	2.1	0.7	0.5	–	–
		3	70	21.8	3.8	2.8	0.9	0.7	–	–
	<1.8 g/cm ³ , <53 μm	1	85.6	9.2	3.6	1.6	–	–	–	–
		2	78	13.9	3.6	2.9	0.8	0.8	–	–
		3	84.9	10.8	1.9	0.5	0.3	1.6	–	–
	<1.8 g/cm ³ , >53 μm	1	94.2	4.8	1	–	–	–	–	–
		2	54.6	44.5	0.9	–	–	–	–	–
		3	96.7	1.8	0.7	–	–	–	–	0.8
Chernozem	1.8–2.0 g/cm ³	1	64.7	29.3	2.6	2	0.8	0.6	–	–
		2	62.6	24.2	4.9	4.7	2.1	1.5	–	–
		3	59.9	37.9	1.6	–	–	0.6	–	–
	<1.8 g/cm ³ , <53 μm	1	86	10.3	1.6	1.3	0.5	0.3	–	–
		2	94.2	4.8	1	–	–	–	–	–
		3	83.2	11.3	2.5	1.7	0.9	0.4	–	–
	<1.8 g/cm ³ , >53 μm	1	75.8	15.1	4.1	2.8	–	1	–	1.2
		2	82.1	14.2	1.7	1.6	–	0.4	–	–
		3	92.1	5.7	1.1	–	–	–	–	1.1

The electron microscopic analysis showed a significantly higher degree of decomposition of organic material than in the free component. An appreciable degree of degradation is observed for the fragments of significantly smaller sizes. Nonetheless, plant residues are well distinguishable. The particles are either encrusted with layered organomineral formations (in most cases, particles of layered minerals, whose surface is covered with OM in the form of F clusters) or represent aggregated structures of these organomineral formations (Fig. 4). The electron microscopic analysis also revealed phytoliths in the LF of soddy-podzolic soil (Fig. 4a).

The analysis of the carbon concentration in the entire fraction revealed a tendency (opposite to that in the free OM) of increasing its mean concentration in this fraction when going from north to south: from 23.5–36.1 wt % for the soddy-podzolic and gray forest

soils to 29.8–42.3 wt % for the chernozems, which is apparently due to their higher degree of humification (Table 2).

The content of nitrogen in the aggregated OM (LF_{agr-1}) in the zonal series of the studied natural soils varies in a significantly narrower range than in the free LF component: from 1.74 to 2.27% of the fraction weight, which can also indirectly indicate the more homogeneous qualitative composition of this LF (Table 2). When going from north to south, the mean nitrogen concentration in the fraction increases from 1.7–2.0 wt % in the soils of the forest cenoses to 2.0–2.2 wt % in the chernozems, which also indicates the higher intensity of humification in the chernozems than in the soddy-podzolic soils.

The comparison of the chemical analysis data with the structures observed in electron microphotos and the microanalysis data (Table 1) showed that the OM

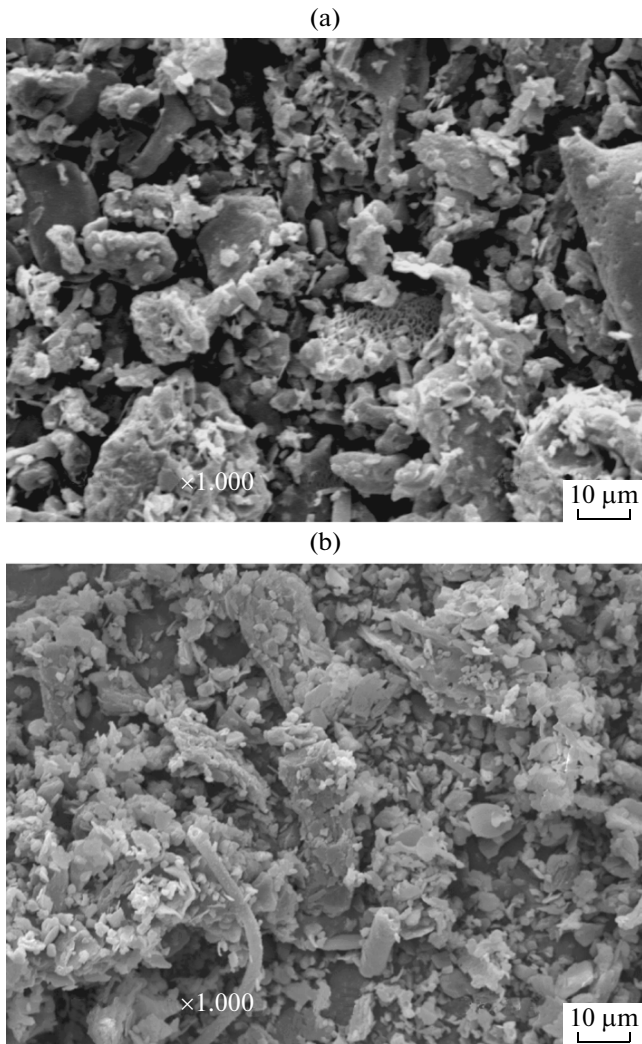


Fig. 4. Images of the light fractions of OM with density $<1.8 \text{ g/cm}^3$ and particle size $<50 \mu\text{m}$ isolated from (a) forest soddy-podzolic soil and (b) chernozem.

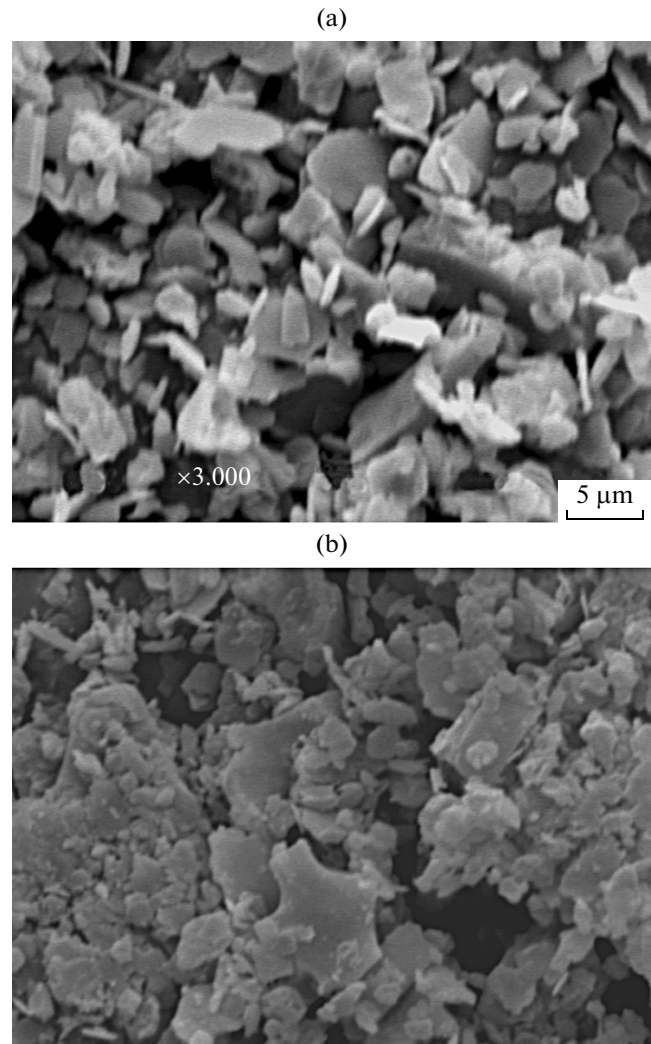


Fig. 5. Images of the light fractions of OM with density $1.8\text{--}2 \text{ g/cm}^3$ isolated from (a) forest soddy-podzolic soil and (b) chernozem.

in this fraction contains selectively preserved and microbiologically transformed plant material. It consists of proper humic substances and products of partial humification of organic residues.

The morphology of the LF with a density of $1.8\text{--}2.0 \text{ g/cm}^3$ ($\text{LF}_{\text{agr-2}}$) significantly differs from those of the lighter fractions: this is a finely dispersed powder, homogeneous in color and in components (brown in color), with a large amount of mineral constituent. It is believed that this fraction is frequently enriched with phytoliths [22–23].

Isolated phytoliths were detected in the soddy-podzolic soil and the chernozem with the electron microscope (Fig. 5). However, it cannot be excluded that all the phytoliths were not identified because of the difficulty of their identification without the removal of OM from them and the soil gels from their surface. This is indirectly confirmed by the abundant

encrustation of biophytoliths (distinguishable in the fraction) with the mineral component (Fig. 5).

The microanalysis data (Table 1) confirm this supposition. The content of silicon in the $\text{LF}_{\text{agr-2}}$ is higher than in the other LFs. At the same time, it can be concluded that the surface of all the particles is covered by the gels incrustated with mineral particles, as is attested to by the presence, along with silicon, of Al, Fe, K, and Mg (3–11, 4–8, 1.5–3.7, and 0.6–1.3%, respectively) in the fraction. These results can be related to either the higher content of SiO_2 in the gels than in the clay minerals or the covering of quartz particles and phytoliths with gels containing clay minerals. The mapping studies confirmed the latter supposition. At the increased content of SiO_2 nanoparticles and clay minerals, the distribution patterns of C, Si, and Al would have coincide. As this was not the case, one can conclude about the existence of heterogeneities on the

Table 2. Carbon and nitrogen contents and ratios in the light and clay fractions from the A1 horizons of the studied natural cenoses in the zonal soil series of the central Russian Plain

Location, object	Depth, cm	C _{tot}	LF _{free}			LF _{agr-1}			LF _{agr-2}			Silt		
			C	N	C/N	C	N	C/N	C	N	C/N	C	N	C/N
ZPS-1	2–10	3.17	38.59	—	—	27.01	—	—	13.06	—	—	6.95	—	—
ZPS-2	3–20	2.29	38	—	—	34.16	—	—	12.75	—	—	6	—	—
ZBS	4–12	2.18	42.9	—	—	36.1	2.27	15.9	13.48	0.89	15.1	13.48	1.64	8.2
Chashnikovo	4–10	2.41	41.54	—	—	28.82	1.74	16.6	16.54	0.85	19.4	10.66	0.88	12.1
Malinki	4–10	3.54	42.44	1.47	28.9	29.88	1.98	15.1	13.85	0.9	15.4	7.57	0.98	7.7
OPKh Bogoslovskoe	6–16	2.79	39.75	2.3	17.3	25.5	1.84	13.8	9.7	0.7	13.8	6.5	0.85	7.6
Kuncherovo	6–21	4.51	33.33	2.44	13.7	29.8	2.18	13.7	11.8	—	—	6.69	1.5	4.5
Poperechenskoe	0–33	7.37	32.42	1.31	24.8	33.87	2	16.9	13.03	1.03	12.6	6.46	1.06	6.1
Ostrovtsy	8–20	6.28	36	2.23	16.1	42.5	2.21	19.2	18.2	—	—	5.31	1	5.3

(Dash) not determined.

microlevel, i.e., on the level of the underlying particles, rather than on the nanolevel.

It follows from the chemical analysis data that the qualitative composition of the OM in this fraction little differs from that in the LF_{agr-1} (Table 2), and the higher density of the fraction can be related to the almost halved content of OM at the similar C/N ratio.

The OM in the clay fractions represents, in the opinion of the authors using the granulodensimetric fractionation of soils [2, 3, 14], a polymineral polydisperse system of the complexes of clay minerals and oxides–hydroxides with humic substances and polysaccharides. The elemental composition of the OM in the clay fractions is similar to that of fulvic acids. A significant relative increase in the content of fulvic acids in the clay fractions compared to the LFs is observed for all the soils [2].

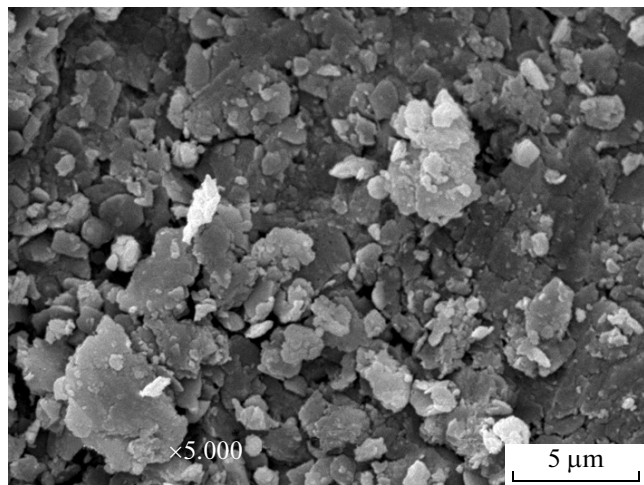


Fig. 6. Image of the clay fraction from forest soddy-podzolic soil.

The microphotos obtained for this fraction show that the morphology of the samples is similar for all the soils. The electron microscopic image obtained for the soddy-podzolic soil is given as an example in Fig. 6. The clay fraction consists of lamellar particles arranged in parallel on the basal planes.

The similarity of such a structure to that of the external surface of the particles covered with soil gels, which is observed in almost all horizons of different zonal soils, is notable [17].

From the earlier stated soil concepts [16], the ultramicroaggregates of clay particles $\leq 1 \mu\text{m}$ in size, which are insufficiently strongly bound by hydrophilic organomineral gels, apparently pass to the clay fraction.

Based on the earlier stated soil concepts [16], we can suppose that the bonds in the hydrophilic colloidal compounds (gels), which link the ultramicroaggregates of clay minerals $\leq 1 \mu\text{m}$ in size to one another, are partially broken under the ultrasonic treatment of the soil samples. This results in their transition to the suspension state.

The following centrifugation of the suspension isolates the mineral particles covered with a dense, more hydrophobic gel layer strongly bound to these particles. The mean density of the particles in the clay fraction is close to the density of water because of the swelling OM, which ensures their retention in the suspended state in water [18]. As a result, ultramicroaggregates of clay mineral particles bound by more hydrophilic gels remain in the suspension after centrifugation. It can be supposed that the method of isolating the clay fraction from soils predetermines the chemical composition of its OM in this case.

Summarizing all the data on the clay fraction—the fulvate composition of the humus, the retention in water when the other fractions are precipitated, and the formation of an external gel layer on the surface of

the soil particles—we can conclude that its behavior is predetermined by the humic substances capable of significant swelling. However, the results of the chemical analysis allowed rectifying our concepts.

Thus, it should be noted that an increase in the concentration of carbon in the clay fraction in the surface horizons is observed in the zonal series of the studied natural soils (Table 2) from 5.3–6.7 wt % (chernozems) to 6.0–13.5 wt % (soddy-podzolic and gray forest soils). This relationship is opposite to the content of minerals with a swelling lattice in the clay fraction: their content does not exceed 10% of the total clay minerals in the soddy-podzolic and gray forest soils and reaches 25–36% in the chernozem [2]. The studies performed on a representative sample set of soddy-podzolic, gray, and chernozemic soils, including arable soils, confirm the earlier revealed correlation between the accumulation of carbon in the clay fraction and its mineralogical composition [13]. It was shown that these two parameters are well correlated with each other: $R = -0.79$ at $P = 0.03$ for the soddy-podzolic soils, $R = -0.82$ at $P < 0.0001$ for the gray forest soils, and $R = -0.95$ at $P < 0.0001$ for the chernozems [1–2].

The C/N ratio in the clay fractions decreases when going from the north to south: from 7.6–12.1 in the soils of the forest cenoses to 4.5–6.1 in the chernozems, which indicates a higher degree of OM humification in the clay fractions of the chernozems (Table 1).

Summarizing all these results, we can conclude that the contents of the clay fraction and three-layer minerals increase but the carbon concentration in the clay fraction and the fulvate content in the humic substances decrease in the zonal series from soddy-podzolic soils to chernozems. These relationships indicate the effect of not only the humic substance but also the three-layer minerals on the content of the clay fraction.

Organic matter in the residual fraction. The fraction represents an accumulation of the coarse fragmentary mineral component, predominantly differently sized fragments of primary minerals, with abundant powdering of the fine-earth component composed of clay minerals (flakes of clay minerals are well distinguished). The OM of the residual fraction includes stable highly aromatic (lignin-like) hydrophobic material, coals, and coal-like substances.

All this perfectly agrees with the proposed mechanism of granulodensimetric fractionation: the OM most strongly bound to mineral particles (fine and medium silt) and, hence, more hydrophobic remains in this fraction. It should be noted that the supposition about the gluing of clay particles by amphiphilic humic substances was advanced earlier [7, 21].

Let us dwell on the statement about the predominant interaction of more hydrophobic humic substances with clay minerals. This is related to the fact that most of the mineral particles in the water environment acquire a negative charge and are surrounded by cat-

ionic atmospheres. The particles of humic substances are amphiphilic: they have irregularly arranged hydrophilic and hydrophobic fragments. The hydrophilic fragments of their particles are also negatively charged because of the great role of carboxylic groups in their formation and are surrounded by cationic atmospheres. The overlapping of similarly charged ionic atmospheres is thermodynamically unprofitable. Therefore, only particles of humic substances with the minimum number of fragments surrounded by ionic atmospheres, i.e., more hydrophobic ones, can approach the surface of minerals (and interact with them).

CONCLUSIONS

(1) It was found that the surface of the soil particles is covered with a gel layer of F clusters.

(2) The obtained results rectify the concepts of the effect of the colloidal component of the organomineral fractions isolated by granulodensimetric fractionation and indicate that the nature of the OM plays a great role in this process.

(3) Our studies confirmed that the light fractions with a density of $<1.8 \text{ g/cm}^3$ and a particle size of $>53 \text{ }\mu\text{m}$ consist of plant residues, but they also contain mineral particles covered with sufficiently thick layers of organomineral films and carbonaceous substances.

(4) In the light fractions with a density of $<1.8 \text{ g/cm}^3$ and a particle size of $<53 \text{ }\mu\text{m}$, along with the selectively preserved and microbiologically transformed plant material composed of proper humic substances and some products of the partial humification of organic residues, phytoliths were also detected.

(5) The clay fraction represents a mixture of ultra-microaggregates and clay mineral particles $\leq 1 \text{ }\mu\text{m}$ in size covered with a hydrophilic organomineral gel.

(6) The OM of the residual fraction contains stable highly aromatic (lignin-like) material, coals, and coal-like substances.

ACKNOWLEDGMENTS

This work was supported in part by the Russian Foundation for Basic Research, project no. 13-04-00140.

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Translated by K. Pankratova