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MINERALOGY AND MICROMORPHOLOGY \_\_\_\_\_

# Mineralogical Composition of Particle-Size Fractions of Solonetzes from the North Crimean Lowland

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Abstract—Data on the mineralogical composition of clay ( $<1 \mu m$ ), fine silt (1–5 µm), medium silt (5–10 µm), and coarser (>10 µm) fractions of meadow solonchakous solonetzes (Calcic Gypsic Salic Stagnic Solonetz (Albic, Siltic, Columnic, Cutanic, Differentic)) developing from loesslike loam and clay in the North Crimean Lowland are presented. Fractions >5 µm constitute nearly 50% of the soil mass and are characterized by the same mineralogical composition in the entire profile; they consist of quartz, plagioclases, potassium feldspars, and micas (biotite and muscovite). The eluvial–illuvial redistribution of clay in the course of solonetzic process is accompanied by changes in the portion of mixed-layer minerals and hydromicas in the upper part of the profile; a larger part of the smectitic phase is transformed into the superdisperse state. In the eluvial SEL horizon and in the illuvial BSN horizon, the clay fraction is impoverished in smectitic phase and enriched in trioctahedral hydromicas. Upon calculation of the content of clay minerals per bulk soil mass, the distribution of mixed-layer minerals is either eluvial, or eluvial–illuvial, whereas the distribution of hydromicas has an illuvial pattern without distinct eluvial minimum in the SEL horizons. The eluvial–illuvial distribution pattern of clay minerals in solonetzes of the North Crimean Lowland is compared with the distribution pattern of clay minerals in solonetzes of the West Siberian Lowland. Coefficients characterizing differentiation of solonetzes by the contents of particular mineral components are suggested.

*Keywords:* mixed-layer minerals, hydromicas, micas, plagioclases, clay fraction, fine silt, medium silt **DOI:** 10.1134/S1064229317120055

#### INTRODUCTION

In Russia, solonetzes and solonetzic soils are found in the forest-steppe, steppe, dry steppe, and semidesert zones with their total area of about 30.8 M ha. Numerous studies are devoted to the genesis, geography, properties, and methods of reclamation of these specific soils. A review of these studies was presented earlier [36]. Solonetzes are developed from parent materials of different geneses and compositions, which creates regional specificity of their properties against the background of common morphological features and major direction of the solonetzic process.

At the qualitative level, data on the mineralogical composition of solonetzes obtained in the 1960s–1980s attest to the eluvial–illuvial distribution of clay in the profile of these soils with the depletion of swelling minerals in the suprasolonetzic (SEL) horizon and their accumulation in the solonetzic (BSN) horizon [8, 18, 31, 34]. At the same time, it is difficult to make

quantitative comparisons of the obtained results because of the use of different methods of calculation of the contents of particular minerals, somewhat different diagnostics of clay minerals (especially, mixedlayer minerals), and the absence of initial experimental data in the form of X-ray diffraction curves in many of the published works. Only three studies were specially devoted to the comparison of data on the mineralogical composition of solonetzes in different parts of Hungary [46], Transvolga region [34], and Western Siberia [41].

Solonetzes in Crimea are mainly found within the North Crimean and Indol lowlands and on the Kerch Peninsula [10, 26, 28]. They are developed from loesslike loams and clays on the lowlands along the Sivash and Karkinit Bay and from the deluvium of Paleogene–Neogene saline clay on the Kerch Peninsula.

In this paper, the genesis and geography of soils of the North Crimean Lowland are discussed on the basis of the results of large-scale soil surveys of local farms [7, 9, 11, 30]. Data on the soil texture, soil salin-

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ity (according to the results of the analyses of soil water extracts), and composition of exchangeable cations are analyzed. The problems of reclamation of Crimean solonetzes under rainfed and irrigation farming systems are considered in a series of works by Novikova [19–24] and Kizyakov [12, 13].

Data on the mineralogical composition of Crimean solonetzes are relatively scarce and have a qualitative character [16, 28]. In loess sediments of Crimea, coarse silt and fine sand fractions are mainly composed of quartz and feldspars [29]; illite predominates among phyllosilicates [32].

The aim of our work is to analyze distribution of minerals in different particle-size fractions along the profile of solonchakous solonetzes developed on silty clay sediments of the North Crimean Lowland.

#### **OBJECTS AND METHODS**

The studied solonetzes are developed on the North Crimean Lowland occupying the northern and northeastern parts of Crimea with absolute heights from 0 to 30–40 m. The surface of the lowland is gently inclined from the Central Crimean elevated plain to the north and northeast towards the Karkinit Bay of the Black Sea in the northwest (the Karkinit Lowland) and the Sivash in the east (the Sivash Lowland); the average slope is 1 m/km. A larger part of the North Crimean Lowland is the zone of the Late Holocene tectonic uplifts with an amplitude of 1.5–2.0 m; coastal parts of the Karkinit Bay and Sivash are the areas of weak modern uplifts and intense salinization processes [3].

The climate of the Karkinit Lowland according to records at the Ishun weather station is very dry, with moderately hot summers and relatively mild winters. The mean annual air temperature is  $9.8-10.5^{\circ}$ C; the mean temperature of the warmest month (July) is  $22.5-23^{\circ}C$ , and the mean temperature of the coldest month (January) is -1.7 to  $-2.4^{\circ}$ C. The average depth of soil freezing in winter is about 30 cm. The accumulated daily temperatures above 10°C reach 3250-3400 degree-days. The duration of the frostless period is 170-186 days. Annual precipitation varies from 340 to 598 mm with the mean value of 362 mm; precipitation during the growing season reaches 195-205 mm with a maximum in July (44 mm). The potential annual evaporation varies within 723-897 mm (with the mean value of 814 mm), and the annual humidity coefficient (the precipitation-to-potential evaporation ratio) is from 0.37 to 0.80 (the mean value is 0.44). This region is characterized by the high frequency of droughts (50-60%).

Within the North Crimean Lowland, parent materials are represented by the silty loesslike loams and clays of the Pleistocene age [3, 4, 9]. The soil cover is composed of chestnut and meadow-chestnut solonetzic soil complexes. The portion of solonetzes and solonetzic soils in these complexes and the degree of soil salinity generally increase toward the coasts of Sivash and Karkinit Bay [7, 9, 28, 30].

Rice systems were created on the North Crimean Lowland in the second half of the 20th century. Water was supplied from the North Crimean channel/ Some parts of the lowland along the coasts remain in the virgin state.

The key site was found in the area of the experimental station of the Department of Soil Science. Reclamation, and Ecology of the Vernadsky Crimean Federal University. It is located on the low sea terrace, 150 m from the coastline of the Karkinit Bay of the Black Seam 2 km to the northwest of the settlement of Kurgannoe in Krasoperekopskii district of the Crimean Republic. The soil cover of this areas consists of crusty (10%), shallow (40%), medium-deep (35%)and deep (15%) meadow chestnut solonchakous solonetzes according to [15]. The groundwater table is found at the depth of 160-180 cm; the concentration of total dissolved solids in the groundwater reaches 30-46 g/L; the salts are of the sulfate-chloride magnesium-sodium composition. The concentration of sulfates is 3-5 times lower than the concentration of chlorides, and the concentration of magnesium is 2.5-3 times lower than the concentration of sodium.

The mineralogical composition of particle-size fractions was studied in two profiles of virgin meadow solonetzes representing a crusty solonetz (pit CR-093) and shallow solonetz (pit CR-092). The morphological description of profile CR-093 is given below. The symbols of soil horizons are given according to the *Field Guide on Correlation of Russian Soils* [27].

Wca, 0-1 cm. Weakly developed humus horizon with dispersed carbonates; light gray (10YR 5/2), dry, silty clay loam, loose fine granular structure; strongly effervescent from the surface; contains fine roots and rhizoids; abrupt smooth boundary; the transition is seen from changes in the effervescence and structure.

SELq, 1-3(7) cm. Eluvial solonetzic (suprasolonetzic) horizon with quasigley features; whitish (10YR 6/2 dry, 10YR 4/3 moist), dry, silty heavy loam, platy structure, no effervescence; contains fine (<1 mm) brown concretions and rounded voids; fine roots; the thickness of the horizon increases between rounded heads of columnar aggregates of the underlying solonetzic (BSN) horizon; clear wavy tonguing boundary; the transition is seen from changes in the color and structure.

BSN1el, 3(7)-10(13) cm. Upper part of the solonetzic horizon with some features of eluviation; dark brown 10YR 3/2 dry), with fine whitish mottles and vertical streaks; slightly dry; silty light clay; compact; with clear columnar structure; the upper side of columns is rounded; their width is about 6-10 cm; upper and lateral sides of columns are covered by whitish skeletans consisting of bleached silty grains; in the deeper part, the skeletans become thinner and less abundant; the columns consist of angular blocky

aggregates covered by clayey coatings; inside the columns, there are fine (2-4 mm) vertically oriented accumulations of silty grains; fine roots; no effervescence; diffuse slightly wavy boundary; the transition is seen from the decrease in the amount of skeletans and whitish accumulations of silty grains and from changes in the structure.

BSN2, 10(13)-18(27) cm. Lower part of the solonetzic horizon; dark brown (coatings, 10YR 4/3; intraped mass, 10YR 5/3); slightly dry; silty light clay; prismatic structure; vertically oriented prisms are 6 to 10 cm in width and consist of the angular blocky-prismatic peds of 1-1.5 cm in size; ped faces are covered by clayey coatings of darker color than the intraped mass; no effervescence; fine roots; abrupt wavy boundary; the transition is seen from the appearance of effervescence.

BCAnc,th, 18(27)-30(32) cm. Carbonate-accumulative horizon with few clayey coatings and with distinct carbonate concentrations; brown (10YR 5/3), with few darker (10YR 4/3) vertical streaks; slightly dry, silty light clay; compact; blocky-prismatic structure with humus-clayey coatings on some of the vertical faces; strongly effervescent; small (1–4 mm) carbonate concentrations; few fine roots; distinct wavy boundary; the transition is seen from the appearance of gypsum veins.

BCAcs, 30(32)-85 cm. Gypsum-containing carbonate-accumulative horizon; light brown (10YR 5/4), lighter than the overlying horizon; wet; sticky; effervescent; a lattice of fine (1–2 mm, up to 3 mm) gypsum veins consisting of fine-granular gypsum; few fine roots; diffuse smooth boundary; the transition is seen from changes in the soil water content and in the form of gypsum accumulation.

BCca,cs,q, 85-155+ cm. Transitional horizon to the calcareous and gypsum-bearing parent material; quasigleyed; yellow-brown (10YR 5/4); satiated wet; sticky silty light clay; strongly effervescent; gypsum crystals are of moderate size (3–6 mm); fine (<1 mm) brown iron nodules.

Soil name.

According to the classification of soils of the Soviet Union [16], this soil is a crusty meadow chestnut solonchakous strongly saline sulfate—chloride clayey solonetz with gypsum developing from the yellowbrown silty clay sediments.

According to the new classification system of Russian soils [15, 29], this a crusty surface-quasigleyed shallow-calcareous gypsum-containing solonchakous strongly saline sulfate—chloride heavy loamy to light clayey solonetz developing from yellow-brown silty clay sediments.

According to WRB-2015 [45], this is a Calcic Gypsic Salic Solonetz (Albic, Siltic, Columnic, Cutanic, Differentic).

The presence of disperse carbonates in a thin surface Wca horizon attests to the beginning of the hydrogenic accumulation of carbonates in the surface layer under conditions of shallow groundwater and intense evaporation from the surface. The profile of pit CR-092 has the following horizonation (depths of the lower boundaries are given in centimeters): Wq,el(2)-SELq(7)-BSN1el,q(16)-BSN2(30)-BSN3(38)-BSN4ca(45)-BCA1q(60) - BCA2q(105) - Bcca.cs(145) - Cca.cs.q(180+).This soil is classified as a crusty meadow chestnut solonchakous strongly saline sulfate-chloride with gypsum clayey solonetz developing on yellow-brown silty clay sediments according to [16], shallow light surface-quasigleved middle-profile-calcareous gypsumcontaining solonchakous strongly saline sulfate-chloride heavy loamy to light clayey solonetz developing from yellow-brown silty clay sediments according to [14, 27], and a Calcic Salic Solonetz (Albic, Siltic, Columnic, Cutanic, Differentic, Bathygypsic) according to [45].

The separation of particle-size fractions (<0.1, 1–5, 5–10 and  $>10 \mu$ m) was performed according to Gorbunov [5] via consecutive complete elutriation procedure. The mineralogical composition was studied by the XRD method with the use of an HZG-4a X-ray diffractometer. Oriented slides saturated with magnesium were analyzed in three states: air-dry, solvated with ethylene glycol for two days, and after 2-h ignition at 550°C. The ratios between major mineral phases in the clay fraction were calculated according to the Biscaye method [42, 43]; in silty fractions, according to Cook with coauthors [44]. The ionic composition of soluble salts was analyzed in standard soil water extracts 1 : 5 [2].

To estimate the degree of differentiation of the upper part of the soil profile between the suprasolonetzic (SEL) and solonetzic (BSN) horizons, coefficients of differentiation  $DD_i$  for particle-size fractions and for particular minerals wre calculated. These coefficients are analogous to the coefficient of illuviation  $N_i$  suggested by Novikova and Kovalivnich [25]. In general, they are calculated according to the following equation:

$$DD_i = \frac{(B-A)}{(A+B)} \times 100,$$

where  $DD_i$  is the coefficient of differentiation according to *i*th component; *A* and *B* are the contents of the *i*th component in the SEL and BSN horizons, respectively; and 100 is the conversion factor to representation of the results in percent.

Positive  $DD_i$  values correspond to a lower content of the *i*th component in the suprasolonetzic horizon in comparison with the solonetzic horizon, whereas negative  $DD_j$  values attest to a higher content of the *i*th component in the suprasolonetzic horizon in comparison with the solonetzic horizon. The range  $-10\% < DD_i < 10\%$  can be the result of measurement and calculation errors; it is taken as an evidence for the

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Horizon	Depth cm	Loss from HCl	Content of fractions, %; fraction size, µm									
HOHZOH	Deptii, ein	treatment	<1	1-5	5-10	>10	<10					
Pit CR-092												
SELq	2-7	0	17.0	16.6	11.6	54.8	45.2					
BSN1el,q	7-16	0	37.7	13.2	8.5	40.6	59.4					
BSN2	16-30	0	48.2	7.6	7.3	37.0	63.1					
BSN3	30-38	0	21.6	23.0	11.4	44.0	56.0					
BCA1q	45-60	17.8	22.4	12.7	9.1	37.9	62.0					
BCA2q	60-85	20.2	27.3	10.3	5.4	36.8	63.2					
BCA2q	85-105	21.2	16.6	14.1	8.8	39.3	60.7					
BCca,cs,q	105-125	19.3	22.9	11.7	8.1	38.0	62.0					
BCca,cs,q	125-145	21.1	19.9	12.5	7.0	39.5	60.5					
Cca,cs,q	165-180	16.5	21.0	13.9	8.5	40.2	59.9					
	$DD_i$		44.4	-25.8	-19.6	-17.6						
		1	Pit CR-0	93	I		I					
SELq	1-3	0	14.5	13.9	13.2	58.4	41.6					
BSN1el	3-10	0	32.0	15.4	7.4	45.3	54.8					
BSN2	10-18	0	36.3	16.8	8.5	38.4	61.6					
BCAnc,th	18-30	9.6	20.1	15.1	8.9	46.3	53.7					
BCAcs	30-50	22.1	23.1	13.0	6.6	35.2	64.8					
BCAcs	50-75	27.3	19.9	11.8	6.6	34.3	65.6					
	$DD_i$		40.6	7.3	-24.5	-16.8						

 Table 1. Particle-size distribution data on solonetzes of the North Crimean Lowland

absence of the soil profile differentiation with respect to the given component. If the component content is less than 2-3% in both horizons, the values of  $DD_i$ were not taken into account, because measurement errors could be comparable with the possible difference in the component contents between the horizons.

The  $N_i$  coefficient suggested by Novikova and Kovalivnich [25] served as the prototype for the  $DD_i$ coefficients. In this paper, we have preserved the original notation  $N_i$  for the clay content (as suggested in [25]); for other mineral components, the  $DD_i$  coefficients are used.

#### **RESULTS AND DISCUSSION**

Loesslike clayey–silty light clay serves as the parent material for the studied solonetzes. Particle-size distribution data on the soil profiles are given in Table 1. Note that the content of the clay (<1  $\mu$ m) fraction in the parent material is about 20–27%. The clay fraction constitutes about one third of the physical clay (<10  $\mu$ m) fraction.

The development of solonetzic process has led to the eluvial—illuvial differentiation of the upper part of the soil profiles. In the suprasolonetzic SELq horizon, the clay content decreases to 14-17% with a simulta-

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neous relative accumulation of particles  $>5 \mu m$  (66– 71% versus 41-49% in the parent material), i.e., medium silt  $(5-10 \mu m)$  and coarse silt and fine sand  $(>10 \ \mu m)$  fractions. In the BSN horizon, the illuvial accumulation of clay up to 32-36% in the crusty solonetz and up to 38-48% in the shallow solonetz is observed. The accumulation of clay in the BSN horizon is confirmed by morphological evidence: abundant continuous clay coatings on peds of different orders. The coefficient of clay differentiation  $N_i$  in both soil profiles is very high (41 and 44%). In the shallow solonetz, it is somewhat higher than in the crusty solonetz. The obtained results are comparable with literature data on solonetzes of the North Crimean Lowland [7, 11, 28] and on the loess sediments of Crimea [29].

The humus content in the suprasolonetzic SEL horizons of the surveyed plots (overall, 21 samples) varies from 1.9 to 3.5% (2.5% on the average); in the solonetzic BSN horizons, from 1.2 to 2.4% (1.6% on the average); in the subsolonetzic calcareous and saline horizons, from 0.4 to 1.0% (0.6% on the average). The accumulation of humus is mainly due to the input of root residues. The total amount of roots of herbaceous plants in the layer of 0-50 cm varies from 24.1 t/ha in shallow solonetzes to 50.8 t/ha in deep solonetzes; up to 67-84% of the total root mass is con-



Fig. 1. Distribution of salts in the profile of crusty solonetz.

centrated in the surface 10-cm-thick soil layer (average data from three replicates) [17].

The salinity assessment of solonetzes at the experimental station was performed in the early 2000s for four major groups of these soils (from crusty to deep solonetzes) [35]; it was also made for soil profiles CR-092 and CR-093 examined in summer 2015. In this paper, we present an averaged (for five soil profiles) salinity plot for crusty solonetzes at the beginning of 2000s (Fig. 1) and combined plots of the vertical distribution of different salinity characteristics (total sum of salts, sum of toxic salts, Cl/SO<sub>4toxic</sub> ratio, and total alkalinity) determined in the water extract from four kinds of solonetzes (overall, five soil profiles were analyzed) (Fig. 2).

The distribution pattern of soluble salts in all the kinds of solonetzes is characterized by their distinct accumulation in the middle part of the profile. The maximum salt content is observed immediately under the BSN horizon in the carbonate-accumulative BCAcs horizon containing the lattice of fine gypsum veinlets (Figs. 2a and 2b). All the horizons below the salt maximum (at 30-40 cm) to the groundwater table (170 cm) are characterized by the strong sulfate-chloride or chloride-sulfate magnesiumsodium salinization with gypsum; the sum of toxic salts reaches 0.5-1.7%. The total alkalinity is increased up to 0.9-1.55 cmol(+)/kg). With an increase in the thickness of the suprasolonetzic SEL horizon from 2–4 cm in the crusty solonetzes to 18– 21 cm in the deep solonetzes, the sum of toxic salts in the layer of 30–120 cm gradually decreases; the sulfate-chloride type of salinization (with the Cl/SO<sub>4-</sub> toxic ratio from 1.0 to 1.9) in the crusty and shallow solonetzes is replaced by the chloride–sulfate salinization ( $Cl/SO_{4toxic}$  0.36–0.68) in the medium-deep and deep solonetzes (Figs. 2b and 2c).

Solonetzic BSN horizons in the crusty, shallow, and medium-deep solonetzes are slightly saline in the upper part (BSN1) and moderately saline in the lower part (BSN2); in the deep solonetzes, both parts are slightly saline. The chemistry of the soil salinization changes in dependence of the salinization degree. Slightly saline horizons (SEL, BSN1, or BSN1+BSN2) are characterized by the chloride—sulfate sodium salinization with an increased alkalinity, whereas moderately saline horizons are characterized by the sulfate—chloride sodium salinization with an increased alkalinity and with the presence of soda in some cases. (Fig. 2d). In all the upper horizons (SEL, BSN) residual sodium bicarbonates are present, which can be judged from positive values of the difference between the total alkalinity and the sum of calcium and magnesium ions in the water extract (Fig. 2e).

The pits examined in 2015 on the same plot have close parameters of the ionic composition of soil water extracts with some variations in the depth of the maximum salinity and salt concentrations. However, an important difference from the earlier obtained data attracts special attention. This is the presence of a thin (1 cm) surface Wca horizon with fine-grained calcite and with some amount of soluble salts exceeding that in the underlying SELq horizon and enriched in chlorides (the Cl/SO<sub>4toxic</sub> ration increases up to 2.2). Such a combination of salinity characteristics attests to the initial stage of the modern secondary salinization of the soil. At present, it is weakly expressed. However, this phenomenon is important, and it is reasonable to present factual data on the salinity of the studied soil pits.

The SEL and BSN do not effervesce with HCl. The depth of effervescence in the soil profiles varies from 18 to 40–45 cm. The distribution of calcium carbonates has its own maximum above 15% at the depths of 40–100 cm. In the parent material, the CaCO<sub>3</sub> content is about 10-12% (Fig. 2f).

The mineralogical composition of the clay ( $<1 \mu m$ ) fraction in the lower soil horizons (the BCA horizon in pit CR-093 at the depth of 18-75 cm and all the horizons deeper than 85 cm in pit CR-092) is characterized by approximately equal portions of mixed-layer minerals (43-50%) and hydromicas (43-48%); chlorite (4-5%) and kaolinite (3-7%) are also present (Table 2, Fig. 3). Randomly interstratified mixedlayer minerals are represented by mica-smectites and chlorite-vermiculites. Hydromicas belong to di- and trioctahedral types. The lower horizons of the two studied profiles of solonetzes somewhat differ in the proportion between these types of hydromicas. In the BCA horizon of the crusty solonetz, the ratio of reflections from X-rays of the first and second orders  $(I_{1.0 \text{ nm}}/I_{0.5 \text{ nm}})$  is about 2.5–2.9, which attests to approximately equal portions of di- and trioctahedral hydromicas. In the shallow solonetz (pit CR-092), the  $I_{1.0 \text{ nm}}/I_{0.5 \text{ nm}}$  ratio is significantly higher: 3.6 to 4.9, which attests to the dominance of trioctahedral hvdromica..

The eluvial-illuvial redistribution of clay in the course of the solonetzic process is accompanied by significant changes in the portions of smectitic phase



**Fig. 2.** Distribution patterns of the (a) total salts, (b) sum of toxic salts, (c)  $Cl/SO_{4toxic}$  ration, (d) total alkalinity, (e) sodium bicarbonates in the water extract, and (f) calcium carbonates in the profiles of the (1) crusty, (2) shallow, (3) medium-deep, and (4) deep solonetzes.

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and hydromicas in the upper horizons; a larger part of the smectitic phase is transformed into the superdisperse state. In the eluvial SELq horizon and illuvial BSN horizon, the portion of the smectitic phase in the

clay fraction considerably decreases, whereas the portion of hydromicas of the predominantly trioctahedral type ( $I_{1.0 \text{ nm}}/I_{0.5 \text{ nm}}$  is from 3.1 to 5.0) increases. The recalculation of these data per bulk soil mass leads us

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Horizon	Dentherm	Clay, %	<i>I</i> <sub>1.0 nm</sub>		Fraction	n <1 μm		Bulk soil mass, %					
	Deptn, cm		$\overline{I_{0.5 \text{ nm}}}$	ML	HM	СН	K	ML	HM	СН	K		
	•			Pit CR-	092				•				
SELq	2-7	17.0	3.4	13*	77	0	11	2.2	13	0	1.8		
BSN1el,q	7-16	37.7	4.8	17*	73	0	9	6.5	27.6	0	3.6		
BSN2	16-30	48.2	4.0	15*	78	0	7	7.4	37.4	0	3.5		
BSN3	30-38	21.6	5.0	23*	68	4	5	5.0	14.7	0.9	1.0		
BCA1q	45-60	22.4	3.7	29	62	5	4	6.5	13.8	1.1	1.0		
BCA2q	60-85	27.3	3.5	29	58	6	6	8.0	15.9	1.7	1.6		
BCA2q	85-105	16.6	4.4	45	46	4	5	7.4	7.7	0.7	0.8		
BCca,cs,q	105-125	22.9	3.6	46	45	4	5	10.6	10.4	0.9	1.1		
BCca,cs,q	125-145	19.9	3.9	50	43	4	3	9.9	8.6	0.7	0.7		
Cca,cs,q	165-180	21.0	4.9	44	48	4	4	9.3	10.1	0.8	0.8		
	$DD_i$	44.4	11.7	9.7	-0.7		-17	52.2	44.2		32		
	I	l	I	Pit CR-	093	I		I	1	I	I		
SELq	1-3	14.5	4.1	27*	65	0	8	3.9	9.4	0	1.1		
BSN1el	3-10	32.0	3.1	35*	60	0	6	11.1	19.1	0	1.8		
BSN2	10-18	36.3	3.9	38	52	4	6	13.7	18.7	1.6	2.3		
BCAnc,th	18-30	20.1	2.9	43	45	5	7	8.7	9.1	1.0	1.4		
BCAcs	30-50	23.1	2.5	45	44	4	6	10.5	10.2	1.0	1.4		
BCAcs	50-75	19.9	2.6	48	43	4	5	9.5	8.5	0.8	1.1		
	$DD_i$	40.6	-7.9	15.1	-7.7	-6.7	7	52.4	33.6				

Table 2. Contents of major mineral phases in the clay (<1 µm) fraction of solonetzes from the North Crimean Lowland

Clay-fractions <1  $\mu$ m,  $I_{1.0 \text{ nm}}/I_{0.5 \text{ nm}}$ -ratio of the intensities of the reflections of first and second orders for hydromicas, ML-mixed-layer minerals, HM-hydromicas, CH-chlorite, and K-kaolinite.

\* Mixed-layer chlorite-vermiculite (smectitic) minerals.

to the following conclusions. First, in the eluvial SEL horizon, the content of smectitic phase decreases by 2.5-4 times in comparison with that in the parent material. Second, in the illuvial BSN horizon, the content of smectitic phase is either the same as in the parent material (in the shallow solonetz), or is 1.1 to 1.3 times higher (in the crusty solonetz). Third, the content of hydromicas in the eluvial SEL horizon is either the same as in the parent material (in the crusty solonetz), or is 1.3 times higher (in the shallow solonetz). Fourth, the BSN horizon of both solonetzes is characterized by the increased content of hydromicas exceeding that in the parent material by 1.8–4.0 times. Fifth, the upper part of the soil profiles does not contain chlorite, i.e., this mineral is subjected to complete destruction in the upper horizons.

The coefficients of differentiation  $DD_i$  demonstrate clear differences between the SEL and BSN horizons independently from their comparison with the parent material. For the smectitic phase in the clay fraction, the  $DD_i$  are positive and relatively small (11.7 and 15.1%), which attests to a lower portion of smectitic phase in the SEL horizon in comparison with the BSN horizon. For hydromicas in the clay fraction, the values of  $DD_i$  are insignificantly small, which means the absence of differentiation of hydromicas in the soil profile. The recalculation of these data per bulk soil mass gives us somewhat different values of  $DD_i$  coefficients. Thus, for the smectitic phase, they reach 52.2–52.4%, which is significantly higher than the values of the  $N_i$  coefficient (40.6 and 44.4%) calculated for the clay fraction. For hydromicas, the values of  $DD_i$ , coefficients (33.6 and 44.8%) are comparable with the values of  $N_i$  coefficients for the same soil profiles.

Such a distribution of clay minerals attests to intensive destruction of the smectitic phase and its transition into the superdisperse state not only in the eluvial (SEL) but also in the clay-illuvial (BSN) horizons. This is accompanied by the relative accumulation of hydromicas leading to the full compensation for their loss in the SEL horizon, or even to their absolute accumulation in this horizon in comparison with the parent material. This is evidently due to the mechanical disintegration of micas in the fine and medium silt fractions with the accumulation of their comminuted fragments and their transformation into hydromicas in the clay fraction. Simultaneously, the absolute accu-



**Fig. 3.** XRD curves for the fraction  $<1 \mu$ m of solonetzes studied in pits CR-093 and CR-092: (*a*) air-dried samples, (*b*) samples treated with ethylene glycol, and (*c*) samples after heating at 550°C for 2 h. Interplanar distances are indicated in nanometers.

mulation of hydromicas in the clay-illuvial BSN horizon takes place.

The profiles of the studied solonetzes are characterized by the approximately even distribution of the fine silt  $(1-5 \mu m)$  fraction. The mineralogical composition of this fraction is the same in both solonetzes. It is represented by micas (32-40%) of the predominantly trioctahedral type (biotite), quartz (28-39%), potassium feldspars (8-11%), plagioclases (7-11%), kaolinite (4-12%), and chlorite (2-7%) (Table 3, Fig. 4). The contents of kaolinite and chlorite in the

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fine silt fraction of the upper horizons (SEL, BSN) are two to three times lower than those in the middle-profile and lower horizons, which may be explained by the mechanical disintegration of the grains of these minerals with their transition into the clay fraction. The fraction of medium silt  $(5-10 \,\mu\text{m})$  displays a tendency for the relative accumulation in the SELq horizon. Deeper, its distribution is relatively even, with small variations. Medium silt consists of the same minerals as fine silt, though the proportions between them are somewhat different. None of the minerals has absolute dominance (Table 4). The content of quartz reaches







37–46%; it is followed by micas (21–26%), plagioclases (13–20%), potassium feldspars (10–13%), kaolinite (2–7%), and chlorite (1–4%). The distribution of minerals in the medium silt fraction along the soil profiles is even. The studied profiles are somewhat different with respect to the crystallographic parameters of micas. In the crusty solonetz (pit CR-093), the  $I_{1.0 \text{ nm}}/I_{0.5 \text{ nm}}$  ratio is 2.2–2.9, which is specified by the presence of both dioctahedral mica (muscovite) and trioctahedral mica (biotite) with a higher portion of the latter. In the shallow solonetz (pit CR-092), the  $I_{1.0 \text{ nm}}/I_{0.5 \text{ nm}}$  ratio varies from 3.0 to 4.3, which attests to the evident predominance of biotite.

The fraction of particles >10 µm mainly consists of the same minerals as the medium silt fraction, except for kaolinite (Table 5). Quartz is the predominant mineral in this fraction; its content reaches 48–64%. The portion of plagioclases also increases (18–23%); a less significant increase is typical of potassium feldspars (10–17%). The contents of mica (5–10%) and chlorite (1–2%) are lower than those in the medium silt fraction. A decrease in the  $I_{1.0 \text{ nm}}/I_{0.5 \text{ nm}}$  ratio (1.9–

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Fig. 4. XRD curves of the fractions of (a) >10, (b) 5–10, and (c)  $1-5 \mu m$  in the air-dried state. Interplanar distances are indicated in nanometers.

2.6; in rare cases, up to 2.9) points to a higher content of dioctahedral mica (muscovite) along with the presence of trioctahedral (biotite) micas.

As noted above, available data on the mineralogical composition of solonetzes in Crimea are mainly of the qualitative character and are based on the obsolete methods of mineral identification; unfortunately, the initial X-ray diffraction curves have not been published [16]. This circumstance does not allow us to compare our data with the earlier published materials.

However, it is possible to compare them with the recently published data on the mineralogical composition of a medium-deep solonchakous solonetz from

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the Sivash Lowland (pit CR-077) [39]. Pit CR-077 was dug on a virgin steppe plot on the Sivash terrace, 1.8 km from the coastline and 2 km to northeast of the Slavyanka settlement of the Nizhnegorskii district of Crimea. The parent material was represented by the loesslike loams and clays. The groundwater table was at the depth of 1.7-2.0.

All the three pits (CR-092 and CR-093 on the Karkinit Lowland and CR-077 on the Sivash Lowland) of solonetzes have similar horizonation (SEL–BSN– BCAcs–BCca,cs) and approximately similar depths of effervescence (18–45 cm; they differ in the thickness of the SEL horizon representing three kinds of

		FS, %	T	Contents of minerals											
Horizon	Depth, cm		$\frac{I_{1.0 \text{ nm}}}{I}$	Q	PL	PFS	М	СН	Κ	Q	PL	PFS	М	CH	Κ
			1 0.5 nm		%	of the	fractic	n			% of	the bu	lk soil	mass	
Pit CR-092															
SELq	2-7	16.6	3.9	34	11	9	40	2	4	5.6	1.9	1.5	6.7	0.3	0.7
BSN1el,q	7-16	13.2	3.3	33	11	10	38	4	5	4.3	1.4	1.3	5	0.5	0.7
BSN2	16-30	7.6	3.0	36	11	8	37	2	6	2.7	0.8	0.6	2.8	0.2	0.5
BSN3	30-38	23.0	2.5	33	9	10	36	4	8	7.5	2.1	2.4	8.2	0.9	1.9
BCA1q	45-60	12.7	3.4	31	9	9	39	4	9	4.0	1.1	1.2	4.9	0.5	1.1
BCA2q	60-85	10.3	3.2	30	7	9	38	6	9	3.1	0.8	0.9	3.9	0.6	0.9
BCA2q	85-105	14.1	2.8	30	9	8	37	5	10	4.3	1.3	1.2	5.2	0.7	1.4
BCca,cs,q	105-125	11.7	2.6	30	10	9	32	7	12	3.6	1.1	1.1	3.8	0.8	1.4
BCca,cs,q	125-145	12.5	2.6	28	9	10	38	6	10	3.5	1.2	1.2	4.7	0.7	1.3
Cca,cs,q	165-180	13.9	3.0	29	9	10	35	7	11	4.0	1.2	1.4	4.8	1.0	1.5
	$DD_i$	-25.8	-11.4	1.2	0	-1.1	-3.4	16.7	16.7	-25.8			-29		
					Pi	t CR-0	093				I				
SELq	1-3	13.9	4.2	39	11	11	32	1	6	5.5	1.5	1.6	4.4	0.1	0.8
BSN1el	3-10	15.4	3.4	34	10	11	37	3	5	5.3	1.6	1.7	5.7	0.4	0.7
BSN2	10-18	16.8	2.9	34	8	11	34	5	9	5.6	1.3	1.9	5.6	0.8	1.4
BCAnc,th	18-30	15.1	3.0	29	10	10	35	6	11	4.3	1.5	1.5	5.2	0.9	1.6
BCAcs	30-50	13.0	2.5	31	10	10	32	6	11	4.1	1.3	1.3	4.2	0.8	1.4
BCAcs	50-75	11.8	2.3	28	10	11	34	6	12	3.3	1.1	1.3	4.0	0.6	1.4
	$DD_i$	7.3	-15.1	-6.8	-10.6	0	5	60.8	8.4	0			12		

Table 3. Contents of major minerals in the fraction 1-5 µm of solonetzes from the North Crimean Lowland

FS-fine silt (1-5 µm) fraction; Q-quartz, PL-plagioclases, PFS-potassium feldspars, M-micas, CL-chlorite, and K-kaolinite.

solonetzes: crusty, shallow, and medium-deep. The degree and chemistry of the soil salinity are also close to one another with some variations in the solonetzic horizon, Important differences are seen in the particle-size distribution patterns. Solonetzes studied on the Karkinit Lowland have a distinct eluvial-illuvial distribution pattern of clay against the background of relatively homogeneous parent materials. The profile of solonetz studied on the Sivash Lowland (pit CR-077) is developed from the three-layered eolian-colluvial loesslike loamy-clayey sediments. The three lithological layers have the same source of material, but differ in the proportions between the particular particle-size fractions and their mineralogical compositions. The eluvial-illuvial differentiation into the SEL and BSN horizons is entirely formed in the upper lithological layer (0-30 cm).

The qualitative composition of clay minerals in the studied soil pits is the same. The major differences are related to the proportion between mixed-layer minerals and hydromicas. In the lower horizons of the solonetz on the Sivash Lowland, the portion of mixedlayer minerals of the mica–smectitic type us higher, and the portion of hydromicas is lower than those in the analogous horizons of solonetzes on the Karkinit Lowland. In all the studied profiles, suprasolonetzic eluvial SEL horizons are characterized by the complete disappearance of mixed-layer mica-smectitic minerals. Mixed-layer chlorite-vermiculitic (smectitic) minerals are partly preserved, and hydromicas and fine-dispersed quartz tend to accumulate. The compositions of the clay fraction in the solonetzic BSN horizons are different. In the Sivash area, mixedlayer mica-smectitic minerals predominate and are partly represented by superdisperse minerals. In the Karkinit area, hydromicas predominate in the clay fraction from the solonetzic horizon.

In the fractions of fine and medium silt, the content of mica of the predominantly trioctahedral type (biotite) in solonetzes of the Karkinit Lowland is higher than that in the solonetz of the Sivash Lowland. As for the minerals in the coarse (>10  $\mu$ m) fraction, their contents in all the studied pits are virtually identical.

The mineralogical composition of clay from the lower horizons of the studied solonetzes in the north of Crimea is close to that in chernozems, meadow chernozems, chestnut soils, and solonetzes developed from loesslike loams and clays [1, 6, 8, 31, 33, 37, 39–41].

			T	Contents of minerals											
Horizon	Depth, cm	MS, %	$\frac{I_{1.0 \text{ nm}}}{I_{0.4}}$	Q	PL	PFS	М	CH	K	Q	PL	PFS	М	СН	Κ
			1 0.5 nm		%	ofthe	fractio	n		% of the bulk soil mass					
Pit CR-092															
SELq	2-7	11.6	4.3	40	20	12	25	1	2	4.7	2.3	1.4	2.9	0.1	0.3
BSN1el,q	7-16	8.5	4.0	45	15	13	23	2	4	3.8	1.2	1.1	1.9	0.1	0.3
BSN2	16-30	7.3	3.4	42	15	12	25	2	3	3.1	1.1	0.9	1.8	0.1	0.2
BSN3	30-38	11.4	3.1	44	11	13	25	2	5	5.0	1.3	1.5	2.9	0.3	0.5
BCA1q	45-60	9.1	3.6	41	15	10	26	3	5	3.7	1.3	0.9	2.4	0.3	0.5
BCA2q	60-85	5.4	4.0	43	17	13	21	2	4	2.3	0.9	0.7	1.1	0.1	0.2
BCA2q	85-105	8.8	3.8	41	13	11	26	3	6	3.6	1.1	1.0	2.3	0.3	0.6
BCca,cs,q	105-125	8.1	3.0	42	15	11	23	3	6	3.4	1.2	0.9	1.9	0.3	0.5
BCca,cs,q	125-145	7.0	3.2	45	15	11	23	1	4	3.2	1.1	0.8	1.6	0.1	0.3
Cca,cs,q	165-180	8.5	3.3	42	14	13	24	2	6	3.6	1.1	1.1	2.0	0.2	0.5
	$DD_i$	-19.6	-8.9	3.8	-14.3	1.6	-1.6			-16					
					Pit (	CR-09	3	-							
SELq	1-3	13.2	2.9	42	18	10	25	2	4	5.6	2.3	1.3	3.3	0.3	0.5
BSN1el	3-10	7.4	2.7	46	15	10	24	2	3	3.4	1.1	0.8	1.8	0.1	0.2
BSN2	10-18	8.5	2.7	42	13	11	23	6	5	3.5	1.1	0.9	1.9	0.5	0.5
BCAnc,th	18-30	8.9	2.2	40	15	10	25	4	6	3.5	1.4	0.9	2.2	0.4	0.5
BCAcs	30-50	6.6	2.3	41	14	10	25	3	7	2.7	1.0	0.7	1.7	0.2	0.5
BCAcs	50-75	6.6	2.4	37	15	12	25	4	7	2.5	1.0	0.8	1.7	0.3	0.4
	$DD_i$	-24.5	-3.6	2.2	-12.9	2.4	-3.1			-23.1					

Table 4. Contents of minerals in the fraction  $5-10 \,\mu m$  of solonetzes from the North Crimean Lowland

MS-medium silt (5-10 µm) fraction; Q-quartz, PL-plagioclases, PFS-potassium feldspars, M-micas, CL-chlorite, and K-kaolinite.

The depletion of mixed-layer minerals from the suprasolonetzic SEL horizon and its relative enrichment in hydromicas in the studied solonetzic of the North Crimean Lowland are close to those observed in the solonetzic soils on the Yergeni Upland [1, 38]. At the same time, these phenomena in the studied solonetzes are less manifested than the analogous phenomena in the solonetzes of the Priobskoe Plateau and, especially, Kulunda Lowland on the West Siberian Plain [40].

As well as in the solonetzes of Western Siberia [40], the accumulation of clay in the solonetzic horizons of the North Crimean Lowland is mainly due to the illuviation of hydromicas and, in some cases, smectitic phase (if calculated per bulk soil mass). The destruction of mixed-layer minerals with smectitic layers and their transition into the superdisperse state are observed in the suprasolonetzic SEL horizon. This is usually (but not always) accompanied by the decrease in the relative portion of these minerals in the clay fraction of the BSN horizon with insignificant changes in their content in the bulk soil mass of this horizon in comparison with the lower-lying horizons. The latter fact contradicts a popular hypothesis about the obligatory illuvial accumulation of swelling minerals in the solonetzic horizon and attests to regional differences in the eluvial—illuvial redistribution of minerals in the solonetzes owing to the initially different contents of smectitic phase in the clay fraction and in the bulk soil mass and to different intensities of the destruction of this phase, its transition into the superdisperse state, and its migration in the soil profiles.

## CONCLUSIONS

(1) In the studied solonetzes of the North Crimean Lowland, the fractions >5  $\mu$ m compose about 50% of the soil mass and are characterize by approximately similar mineralogical composition along the soil profiles with a small relative accumulation in the eluvial SEL horizon and their even distribution in the rest part of the profile. They consist of quartz; plagioclases; potassium feldspars, whose content is higher in the coarse fractions and decreases with a decrease in the size of silt particles; they also contain micas (biotite and muscovite), chlorite, and kaolinite, whose contents increase with a decrease in the size of soil particles.

		Res., %	$\frac{I_{1.0 \text{ nm}}}{I}$	Contents of minerals										
Horizon	Depth, cm			Q	PL	PFS	М	CH	Q	PL	PFS	М	СН	
			10.5 nms		% of	the frac	tion	•		% of the	e bulk so	il mass		
Pit CR-092														
SELq	2-7	54.8	2.2	64	18	12	5	1	35.1	9.8	6.4	2.6	0.4	
BSN1el,q	7-16	40.6	2.3	61	22	10	5	2	24.7	8.7	4.0	2.1	0.8	
BSN2	16-30	37.0	2.6	58	17	15	8	1	21.5	6.2	5.4	3.0	0.4	
BSN3	30-38	44.0	2.7	55	20	16	6	2	24.1	8.8	7.2	2.7	0.7	
BCA1q	45-60	37.9	2.8	59	21	10	6	1	22.5	8.0	3.8	2.4	0.5	
BCA2q	60-85	36.8	2.9	51	22	19	6	2	18.8	8.0	6.8	2.1	0.6	
BCA2q	85-105	39.3	1.9	61	19	12	6	1	23.9	7.4	4.5	2.4	0.3	
BCca,cs,q	105-125	38.0	2.9	52	21	14	8	2	19.9	8.1	5.2	3.2	0.7	
BCca,cs,q	125-145	39.5	2.7	51	23	15	8	1	20.2	8.9	6.1	3.3	0.4	
Cca,cs,q	165-180	40.2	2.1	48	28	15	6	1	19.5	11.2	6.0	2.4	0.4	
	$DD_i$	-17.6	6.4	-3.9	2.7	4	15.3		-21.2	-15.3	-13.3			
		•			Pit CR	-093		•	•	•	•			
SELq	1-3	58.4	2.2	59	19	12	8	2	34.2	11.1	6.7	4.6	1.1	
BSN1el	3-10	45.3	4.1	57	25	11	6	1	25.7	11.2	4.8	2.7	0.5	
BSN2	10-18	38.4	2.2	51	22	16	8	2	19.7	8.4	6.2	2.9	0.6	
BCAnc,th	18-30	46.3	2.1	53	19	14	9	2	24.6	8.9	6.4	4.3	0.9	
BCAcs	30-50	35.2	2.6	50	18	17	9	2	17.5	6.4	6.1	3.3	0.8	
BCAcs	50-75	34.3	2.2	54	21	13	10	1	18.4	7.2	4.4	3.3	0.2	
	$DD_i$	-16.8	17	-4.6	10.4	6.6	-6		-20.6	-6.7	-10	-24.3		

**Table 5.** Contents of minerals in the fraction  $>10 \,\mu m$  of solonetzes from the North Crimean Lowland

Res.—residue after the removal of clay and fine and medium silt (fractions >10  $\mu$ m); Q—quartz, PL—plagioclases, PFS—potassium feldspars, M—micas, CH—chlorite, K—kaolinite; tr—trace amounts.

(2) The eluvial-illuvial redistribution of the clay fraction in the course of solonetzic process is accompanied by noticeable changes in the portions of smectitic phase and hydromicas in the upper horizons of the profile; a larger part of the smectitic phase in these horizons acquires the superdisperse state. In the eluvial SEL and clay-illuvial BSN horizons, the portion of the smectitic phase in the clay fraction is decreased, whereas the portion of hydromicas of the predominantly trioctahedral type is increased. Upon recalculation of the contents of minerals per bulk soil mass, the distribution of mixed-layer minerals displays either an eluvial or an eluvial-illuvial pattern, whereas the distribution of hydromicas has a distinct illuvial pattern without their minimum in the eluvial SEL horizon.

(3) The eluvial-illuvial redistribution of clay minerals in solonetzes of the North Crimean Lowland is stronger pronounced in comparison with that in solonetzes of the Baraba Lowland characterized by a higher content of the smectitic phase and is less pronounced in comparison with solonetzes of the Priobskoe Plateau and Kulunda Lowland, in which mixed-layer minerals are almost totally destroyed both in the eluvial and illuvial horizons.

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