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Electron microscope study of NaCl- and Pb(CH_3COO)$_2$-treated kaolinite**

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Abstract. The interaction of NaCl and Pb(CH_3COO)$_2$ with kaolinite was studied using scanning electron microscopy (SEM). Multiple ordered stacks or 'quasi-crystals' (up to 1 μm in diameter and up to 2 μm in height) and their assemblies (up to 10 μm in size) have been detected under treatment of kaolinite with NaCl-solution. 'Quasi-crystals' are symmetrically ordered stacks in which equal in size kaolinite platelets are packed plane to plane. The one-dimensional orientational and translational order is assumed to be strong within the stacks, along the axis of the stacks, whereas the symmetry is breaking when leaving a given stack and passing from one stack to another in assemblies of 'quasi-crystals'. The 'quasi-crystals' of NaCl-treated kaolinite are partially preserved after dialysis. Under treatment of kaolinite with Pb(CH_3COO)$_2$ flat 'quasi-crystals' are formed from original kaolinite particles packed edge to edge, from 1 to 3 μm in size and their textured aggregates up to 7 μm in size. 'Quasi-crystals' in textured aggregates are packed plane to plane with a shift. Neoformations of Pb(CH_3COO)$_2$-kaolinite are metastable to dialysis.

Keywords: kaolinite, NaCl, Pb(CH_3COO)$_2$, scanning electron microscopy

INTRODUCTION

Water-soluble salts considerably affect the structure, surface properties and water vapour sorbing capacity of soils and clay minerals. Treatment of soils and clay minerals with NaCl leads to an increase in their waterholding capacity and to the formation of a crust and cracks at drying (Rode, 1965; Tarasevich, 1988). Our investigations showed that kaolinite treated with NaCl also differs from the original kaolinite having abnormally high water vapour sorption capacity at the area of capillary condensation (Kharitonova *et al.*, 2002). The elimination of excess salt with dialysis causes a sharp decrease of its water vapour sorption capacity. On the contrary, kaolinite treatment with Pb(CH_3COO)$_2$ causes a sharp decrease of water vapour sorption capacity. After dialysis, kaolinite sorption isotherms practically coincide with sorption isotherms of the original kaolinite (Manucharov *et al.*, 2001). Therefore, changes in kaolinite due to treatment with the salts NaCl and Pb(CH_3COO)$_2$ present an interesting topic to explore. In this respect the use of highly-localized investigation methods like modern electron microscopy seems quite promising. Electron diffraction method allows us to study the surface layers of solid crystals. Unlike the X-rays, which deeply penetrate the crystal, the electron beam is fully reflected from the surface layers. The objective of this study was to determine the causes of the change in the surface properties of kaolinite affected by NaCl and Pb(CH_3COO)$_2$ using a complex of transmission and scanning electron microscopy methods. Specifically we intended to test the following hypotheses:

1. Structural reorganization of kaolinite particles under kaolinite treatment with NaCl as well as with Pb(CH_3COO)$_2$.
2. Hypothetically, new formations of NaCl-kaolinite should have certain differences in structure and qualities compared to Pb(CH_3COO)$_2$-kaolinite.

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MATERIALS AND METHODS

A monomineral sample of kaolinite was obtained from the museum of the Department of Soil Physics and Reclamation, Faculty of Soil Science, Moscow State University. NaCl- and $Pb(CH_3COO)_2$-treated mineral specimens were obtained by treatment of 10 g samples of original natural mineral, triturated to the particle size less than 0.074 mm, in 200 ml of a 1 N solution of a corresponding salt. The suspension was shaken with a rotator for 6 h and filtered. Afterwards, the specimens were dried to the air-dry state, and triturated again to the particle size less than 0.074 mm. Then several specimens of the initial kaolinite and NaCl- and $Pb(CH_3COO)_2$-treated kaolinite specimens were dialyzed, and the rest were washed with distilled water.

The transmission electron microscope 'Tesla BS-613', having acceleration voltage of 80 kV, was used for TEM microphotography and electron microdiffraction of kaolinite specimens. The magnification of electron-transparent images was 10000. The scanning electron microscope 'LEO EVO 40 HV' (Carl Zeiss, Germany) was used for SEM imaging; magnification was from 1000 up to 100000. In the first set of experiments kaolinite specimens were prepared for electron microscopy imaging with standard methods – the suspension method with distilled water as dispersion medium for TEM, and sprinkling of powder on the holder with silver paste for SEM (Chi Ma and Eggleton, 1999). In the second set of EM experiments we used C_2H_5OH as dispersion medium for preparation of kaolinite specimens. Nearly 500 photos were recorded during this study, providing a significant number (~100) of interpretable images.

Bulk content of Na and Pb was determined with an 'ORTEC' analyzer TEFA-III (Savichev and Sorokin, 2002). Exchangeable cations in all specimens were determined by modified Pfeiffer method taking into account the effect of soluble salts (Manual for Laboratory Methods of Studying the Salt-Ion Composition of Neutral and Alkaline Soils, 1990).

RESULTS AND DISCUSSION

Data of the first set of experiments showed that NaCl-kaolinite specimens revealed no changes in particle organization in a clay mineral. Only single textured aggregates were identified in $Pb(CH_3COO)_2$-kaolinite specimens. The reason for that was the high solubility of NaCl and $Pb(CH_3COO)_2$ in water (TEM) and the uneven distribution of thin kaolinite particles (SEM). Apparently, at the preparation stage (several drops of specimen suspension dissolved in water are taken for the TEM experiment), salt excess dissolved and the sample changed. Therefore, we had to modify the preparation method. We used C_2H_5OH as dispersion medium, in which NaCl and $Pb(CH_3COO)_2$ solubility is low (0.1 g 100 g^{-1} and 3.5 g 100 g^{-1} C_2H_5OH, respectively). Specimens for the SEM were prepared using alcohol suspension as in the case of the TEM.

The use of C_2H_5OH as dispersion medium when preparing the NaCl-specimen for TEM helped to observe single lamella aggregates of kaolinite particles up to 1 μm in size. Like lamella aggregates of $Pb(CH_3COO)_2$-kaolinite described before (Kharitonova *et al*., 2004), lamella aggregates of NaCl-kaolinite are not symmetrical; they are of irregular form, partially electron transparent with electron nontransparent inclusions. Original kaolinite is characterized by separate electron nontransparent hexagonal-like particles with sharp edges and electron transparent particles with weathered edges. Both kinds of particles are >0.25 μm in size and can be observed in conglomerates. Electron diffraction patterns of initial kaolinite specimen of all experimental sets are circular. The electron-diffraction pattern of the central part of the lamella aggregate is diffuse, transitional from a circular to a dotted electron diffraction pattern, and evidently different from electron diffraction patterns of the initial kaolinite and NaCl (Chukhrov and Bronshtedt-Kupletskaya, 1963), thus indicating the 'plane-to-plane' aggregation of kaolinite particles.

Scanning electron microscopy examinations of kaolinite specimens, prepared with suspension in C_2H_5OH method, indicated that under specimen treatment with NaCl kaolinite particles are packed plane to plane. Numerous 'quasi-crystals', up to 1 μm in diameter and 2 μm in height (Fig. 1), and assemblies of quasi-crystals, up to 10 μm in size, were identified. 'Quasi-crystals' are symmetrically ordered stacks, in which the kaolinite platelets of similar size are in close contact, being separated from each other only at the edges. The one-dimensional orientational and translational order is assumed (Van Damm, 1998) to be strong within the stacks, along the axis of the stacks, whereas the symmetry is breaking when leaving a given stack and passing from one stack to another in assemblies of 'quasi-crystals'. Initial kaolinite specimens constitute separate rigid platelets and aggregates with 'ideally porous' architecture, in which rigid platelets are randomly packed. After 'quasi-crystals' were found in specimens prepared with the method of suspension in alcohol, similar neoformations were identified in specimens prepared with the method of sprinkling of powder, although their images are less distinct, and quasi-crystals and their assemblies are masked with fine and flat kaolinite particles. It was difficult to single them out at the first stage of analysis, as their structure had not been defined yet. Thus, the SEM method, applied to study surface characteristics of kaolinite, turns out to be more informative than the TEM method.

Simultaneous SEM examinations of $Pb(CH_3COO)_2$-kaolinite specimens with SE- and QBSE-detector (detector of second and back scattered electrons, respectively) revealed more details of changes in kaolinite particle organization under treatment with $Pb(CH_3COO)_2$. First of all, the use of QBSE-detector significantly speeded up and facilitated the search of $Pb(CH_3COO)_2$-kaolinite neoformations as compared

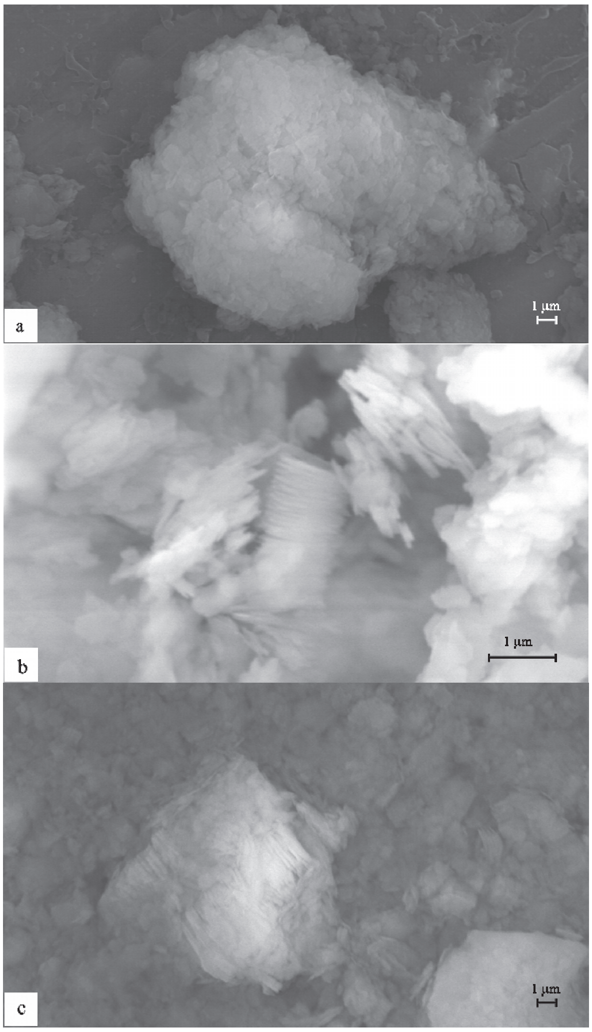

Fig. 1. SEM images (SE detector) of kaolinite samples: a – original kaolinite; b – sample treated with NaCl, 'quasi-crystal'; c – sample treated with NaCl, assembly of 'quasi-crystals'.

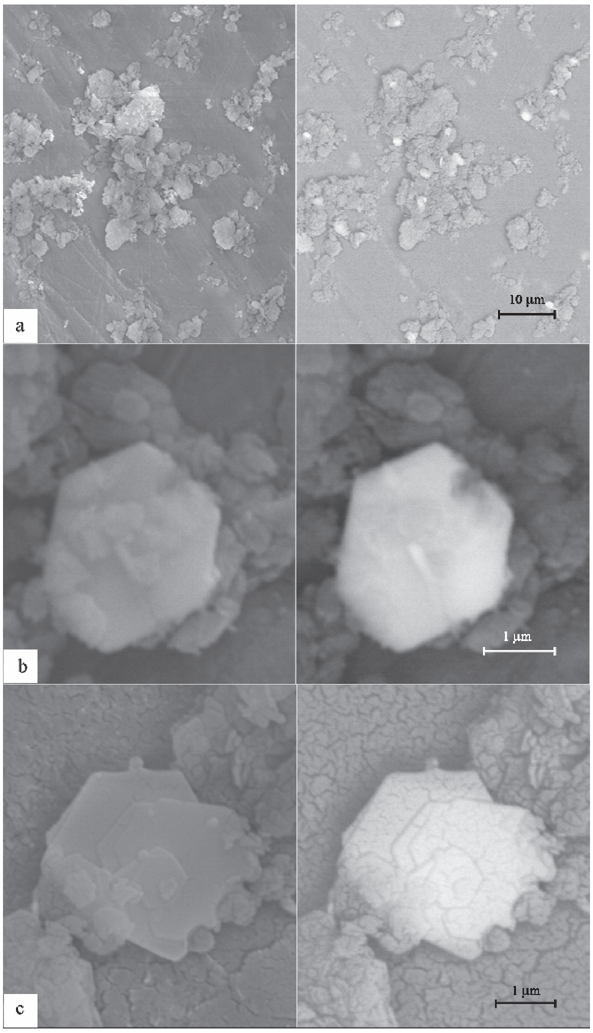

Fig. 2. SEM images of kaolinite treated with $Pb(CH_3COO)_2$: a – sample in full; b – 'quasi-crystal'; c – assembly of 'quasi-crystals' (the left images – SE-detector, the right images – QBSE-detector).

with NaCl-ones. When QBSE-detector was applied in phases with a bigger average atomic number (atomic number of lead is 82), these phases were found to be brighter in contrast to phases with a smaller average atomic number (Fig. 2). Secondly, scanning electron microscopy examinations of kaolinite specimens treated with 1 N solution of $Pb(CH_3COO)_2$ revealed numerous flat 'quasi-crystals', from 1 to 3 μm in size, and their textured aggregates of up to 7 μm in size (Fig. 2). The newly formed flat and hexagonal in shape 'quasi-crystals' of $Pb(CH_3COO)_2$-kaolinite are composed of initial kaolinite particles, aggregated edge to edge. Figure 2b shows a 'quasi-crystal' of a nearly ideal hexagonal shape with a missing element of a flat structure. Figure 2c clearly shows that one of the hexagonal edges misses presumably three particles (about 0.25 μm in size) of the initial kaolinite. In textured aggregates 'quasi-crystals' of $Pb(CH_3COO)_2$-kaolinite are aggregated plane to plane with a shift. The number of single 'quasi-crystals' in a textured aggregate does not exceed 7, whereas the number of single platelets in a stack of Na-kaolinite is over 20.

Bulk X-ray-fluorescent analysis revealed that Na (as Na_2O) and Pb contents in salt-treated kaolinite are much more than for initial kaolinite (0.49 and 0.23%, 98.2 and 0.1 mg g^{-1} of air-dry mineral, respectively). Thus the formation of lamella aggregates in NaCl- and $Pb(CH_3COO)_2$-kaolinite is attributed to the effect of the salt treatment. QBSE-detector images provided another evidence that cations of Pb participate in the structure of $Pb(CH_3COO)_2$-kaolinite neoformations and textured aggregates which appear more distinct as compared to other particles (Fig. 2).

T a b l e 1. Composition of exchangeable cations in initial kaolinite, NaCl- and $Pb(CH_3COO)_2$-kaolinite, meq 100 g^{-1} of air-dry mineral

Mineral and saturated salt		Ca	Mg	Na	K	Zn	Pb	Sum
Kaolinite	O*	6.59	1.83	1.19	0.13	0	0	9.74
	OD	3.80	1.37	0.48	0.38	0	0	6.03
	OW	1.32	0.60	0.06	0.06	0.05	0	2.09
NaCl	S	0.67	0.25	3.58	0.10	0	0	4.60
	SD	0.53	0.60	1.52	0.15	0	0	2.80
	SW	1.23	0.32	1.64	0.09	0.02	0.01	3.31
$Pb(CH_3COO)_2$	S	0.54	0.85	0.11	0.06	0.06	0.05	1.67
	SD	1.76	1.17	0.26	0.13	0	0.06	3.38
	SW	1.24	0.92	0.17	0.10	0.01	0.02	2.46

*O – initial kaolinite, S – kaolinite treated with corresponding salt, D – dialyzed and W – washed forms of O – and S – kaolinite, respectively.

As NaCl and $Pb(CH_3COO)_2$ are water-soluble salts, so it could be assumed that the neoformations of NaCl- and $Pb(CH_3COO)_2$-kaolinite must disintegrate after dialysis and washing with water. Scanning electron microscopy examinations showed that this happened in the case of $Pb(CH_3COO)_2$-kaolinite, whereas SEM images of NaCl-kaolinite after dialysis revealed partially preserved neoformations. Data on analysis of the exchangeable cation composition (Table 1) also support the SEM data on the effect of dialysis and washing with water on the kaolinite neoformations stability. Dialysis of NaCl-kaolinite does not affect the content of exchangeable Ca (0.5-0.7 meq 100 g^{-1}). Apparently, under NaCl treatment of kaolinite Na cations take positions more stable with respect to dialysis, probably like Pb cations (Businelli *et al*., 2003) take the positions of exchangeable Ca. Only after NaCl-kaolinite is washed with water, the content of exchangeable Ca increases and nearly reaches the content of exchangeable Ca in the initial kaolinite washed with water and in $Pb(CH_3COO)_2$ -kaolinite after dialysis and washing with water. The exchangeable Ca contents of $Pb(CH_3COO)_2$-kaolinite increases both after specimens dialysis and washing with water (from 0.5 to 1.8 and 1.2 meq 100 g^{-1}, respectively). These data may indicate partial preservation of exchangeable Ca^{2+}-cations in interplatelet space of NaCl- and $Pb(CH_3COO)_2$-kaolinite. After destruction of neoformations with dialysis, blocked Ca^{2+}-cations become exchangeable. The permanent dipole structure of kaolinite particles (Kukovsky, 1966) seems to cause lamella aggregation of kaolinite particles under treatment with the salts NaCl and $Pb(CH_3COO)_2$. Symmetrical 'quasi-crystals' are formed when kaolinite is treated with a solution of NaCl, a strong electrolyte. Less symmetrical and less stable lamella aggregates are formed in the medium of a weak electrolyte, $Pb(CH_3COO)_2$ (Nekrasov, 1973).

CONCLUSIONS

1. Scanning electron microscopy studies revealed considerable changes of kaolinite aggregate architecture after treatment with the salts NaCl and $Pb(CH_3COO)_2$. The aggregation of original kaolinite particles was observed. Particle aggregation type and the stability of newly formed kaolinite aggregates depend on specific properties of salt treatment.

2. Kaolinite treatment with NaCl causes the formation of numerous 'quasi-crystals', up to 1 μm in diameter and 2 μm in height, and assemblies of quasi-crystals, up to 10 μm in size. 'Quasi-crystals' are the symmetrically ordered stacks in which equal-size kaolinite platelets are packed plane to plane. The one-dimensional orientational and translational order is strong within the stacks, along the axis of the stacks, whereas the symmetry is breaking when leaving a given stack and passing from one stack to another in assemblies of 'quasi-crystals'. The 'quasi-crystals' of NaCl-kaolinite are partially preserved after dialysis.

3. When kaolinite is treated with $Pb(CH_3COO)_2$ flat quasi-crystals from 1 to 3 μm in size and aggregated edge by edge, and their aggregates up to 7 μm are formed from initial kaolinite particles. 'Quasi-crystals' in textured aggregates are packed plane to plane with a shift. Neoformations of $Pb(CH_3COO)_2$-kaolinite disintegrate after dialysis.

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