

## Interaction of $Pb^{2+}$ and $Zn^{2+}$ salts with clay minerals\*\*

G.V. Kharitonova<sup>1\*</sup>, A.S. Manucharov<sup>2</sup>, N.P. Chizhikova<sup>3</sup>, V.N. Zemlyanukhin<sup>4</sup>,  
and N.I. Chernomorchenko<sup>2</sup>

<sup>1</sup>Institute of Aquatic and Ecological Problems, Far East Division, Russian Academy of Sciences,  
65 Kim-Yu-Chen Str., Khabarovsk, 680000 Russia

<sup>2</sup>Faculty of Soil Science, Moscow State University, Vorob'evy gory, Moscow, 119899 Russia

<sup>3</sup>Dokuchaev Soil Science Institute, 7 Pyzhevsky per., Moscow, 119899 Russia

<sup>4</sup>Institute of Tectonics and Geophysics, Far East Division, Russian Academy of Sciences, 65 Kim-Yu-Chen Str., Khabarovsk,  
680000 Russia

Received January 5, 2004; accepted February 18, 2004

**A b s t r a c t.** Multiple mica-like monocrystals, 3  $\mu\text{m}$  in size, are formed when smectite is saturated with 1N  $Pb(CH_3COO)_2$  solution. The appearance of neoformations meta-stable to water may be attributed to inner-sphere complex of  $Pb^{2+}$  cations and smectite macroanion with its charge being centered in the tetrahedral layer of beidellite structure. Textured aggregates and few neo-formation monocrystals are found in  $Pb(CH_3COO)_2$ -saturated kaolinite specimens. No changes of particle organization in clay minerals saturated with 1N  $ZnCl_2$  solution are registered.

**K e y w o r d s:** Pb, Zn, clay minerals, electron microscopy, X-ray diffraction

### INTRODUCTION

The most important distinctive feature of clay minerals is their ability to balance with geochemical conditions. Clay mineral stability in changing environment is the function of their origin, structure, elementary cell charge and dispersion. Smectite is considered to be the most changeable and kaolinite is the most stable. Thus it seems of current interest to evaluate changes in clay minerals due to saturation with salts whose cations have similar chemical characteristics but differ substantially in radii, hydration behaviour, and strength of bond with ion-exchange centers of clay minerals surface.

According to the character of interaction with different ligands, lead and zinc are classified as intermediate acceptors between hard and soft Lewis acids (Moor and

Ramamoorthy, 1984). But in water media,  $Pb^{2+}$  cations mostly form inner-sphere complexes with surface functional groups, whereas  $Zn^{2+}$  cations form outer-sphere complexes *ie* they are connected with ligand functional groups through water molecules (Pinsky, 1997; Apozito, 1981).  $Pb^{2+}$  cations are less hydrated and more strongly connected with ion-exchange surface centers as compared to zinc cations (Förstner and Wittmann, 1983). As  $Pb^{2+}$  radius is similar to the radius of  $K^+$ , interlayer cation in clay minerals of illite group (0.132 and 0.133 nm, respectively,  $Zn^{2+}$  cation radius of 0.083 nm is much less (Nekrasov, 1973)), it may be assumed that mica-like structures are formed during  $Pb^{2+}$  cations saturation of clay minerals with 2:1 layers. In nature, lead is known to be present in mica, usually in high concentrations (Hawkes and Webb, 1962). Formation of similar complexes in kaolinite, a clay mineral with rigid structure and zero charge in structure layers 1:1, does not seem possible (Cotton and Wilkinson, 1965).

This study attempts to clarify the nature of changes in clay minerals like smectite and kaolinite, when they are saturated with Pb and Zn salts. Electron microscopy (microphotography and electron microdiffraction) and X-ray diffraction methods served our purpose.

### MATERIALS AND METHODS

The smectite and kaolinite samples studied were granted by the museum of the Department of Soil Physics and Amelioration Department, Faculty of Soil Science,

\*Corresponding author's e-mail: dmitry@ivep.khabarovsk.ru

\*\*This work was supported by the Russian Foundation for Basic Research (Project No. 03-04-48370).

Moscow State University.  $\text{ZnCl}_2$  and  $\text{Pb}(\text{CH}_3\text{COO})_2$ -saturated smectite and kaolinite specimens were compared with respective original natural minerals. Salt-saturated clay minerals were obtained by saturation of 10g samples in 200 ml of 1N solution of a corresponding salt. The suspension was shaken with a rotator for 6 h and then sediments were filtered (experiment series 1 - saturation). Specimens of series 1 were subjected to dialysis in experiment - series 2.

An electron microscope 'Tesla BS-613' (acceleration voltage - 80 kV) was used for transmission microphotography and electron microdiffraction of natural samples of clay minerals and their modified forms. Specimens for electron microscopy were prepared by suspension method with distilled water as dispersion media, collodion as support. Magnification of electron-transparent images was 10000. To obtain diffraction traces of clay mineral samples, a versatile X-ray diffractometer HZG-4A (Carl Zeiss Jena, Germany) with a  $K\alpha\text{Cu}$ -target tube and a Ni filter was employed. Its operating regime was the following: tube voltage of 40 kV, anode current of 30 mA and goniometer rotation velocity of  $2^\circ \text{ min}^{-1}$ . X-ray diffraction traces were taken for oriented specimens deposited on cover glasses. To clarify the details of clay minerals structure, specimens were saturated with  $\text{K}^+$  cations by Weaver method (Weaver, 1958) and with  $\text{Li}^+$  cations by Green-Kelly method (Green-Kelly, 1953). Bulk content of Zn and Pb was determined with an 'ORTEC' analyzer TEFA-III (Savichev and Sorokin, 2002). To acquire comparable data, exchangeable cations in all clay specimens were determined by modified Pfeiffer method, which allowed to take into account the effect of soluble salts (Manual for Laboratory Methods of Studying the Salt-Ion Composition of Neutral and Alkaline Mineral Soils, 1990).

## RESULTS AND DISCUSSION

Transmission electron microscopy (TEM) examinations of smectite specimens saturated with 1N solution of  $\text{Pb}(\text{CH}_3\text{COO})_2$  revealed numerous crystalline neoformations, 3  $\mu\text{m}$  in size, and xenomorphic electron-nontransmitting accumulations of 'glued' smectite crystallites (Fig. 1a). The neoformation crystals are electron-transparent, tabular and hexagonal, of short-prismatic shape with distinct edges. Initial smectite constitutes a cloud-like conglomeration of fine irregularly oriented fibrous crystallites 0.15-0.40  $\times$  0.015-0.035  $\mu\text{m}$  in size (Chukhrov, 1992). The TEM image of the neoformation crystal examined clearly shows that not fully structured and vague adjacent faces of one of the vertical hexagon edges consist of nontransparent smectite particles, which are not completely transformed. Electron microdiffraction of the central part of the crystal results in a dotted pattern, which proves monocrystal character of these neoformations. A 'not completely structured fragment' of a crystal is characterized by a less symmetric electron-diffraction

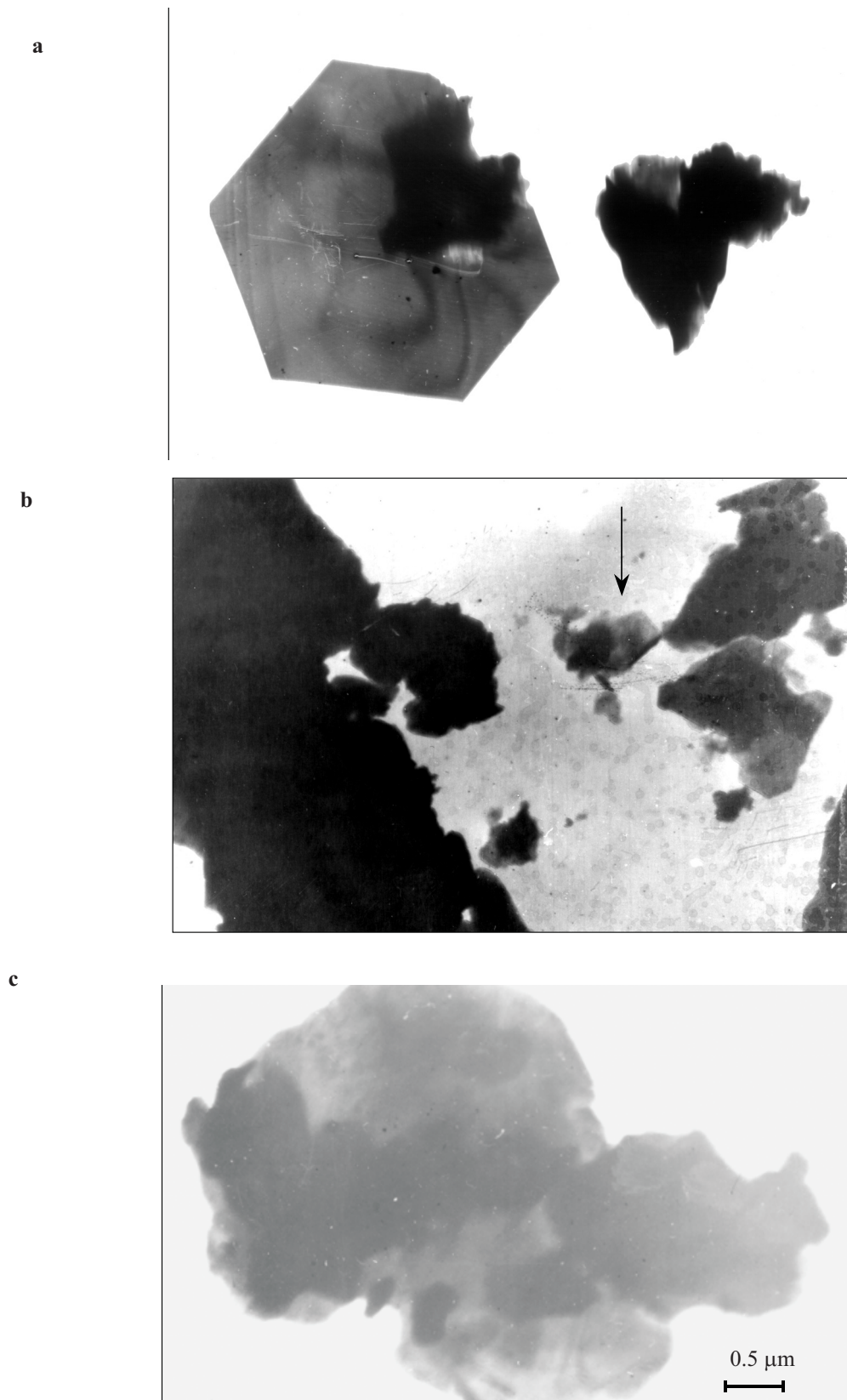
pattern. Neoformation crystals with substantially disturbed structure, hexagonal in form, produce transitional (from dotted to circular) electron-diffraction patterns. Specimens of initial untreated smectite and of  $\text{Pb}(\text{CH}_3\text{COO})_2$ -saturated smectite produce circular electron-diffraction patterns as a whole (Kharitonova *et al.*, 2002).

Average lattice parameters of new-phase monocrystals within the accuracy of observation are as follows: ' $a_0$ ' =  $0.521 \pm 0.008$  nm, ' $b_0$ ' =  $0.893 \pm 0.008$  nm, angle  $\beta \approx 100^\circ$ . They coincide with respective smectite parameters ' $a_0$ ' = 0.517 nm, ' $b_0$ ' = 0.897 nm, angle  $\beta \approx 99^\circ 54'$  (Chukhrov and Smol'yaninova, 1992). A not completely structured fragment of a monocrystal is characterized by the same values of ' $a_0$ ' and ' $b_0$ ' but the angle  $\beta$  is much bigger and equals  $110^\circ$ . The 0.334 nm reflex is absent in the initial smectite, but is present in electron-diffraction patterns of monocrystals and a not completely structured fragment. This reflex may be considered as indicative of a mica-like structure peculiar to monocrystals as a whole.

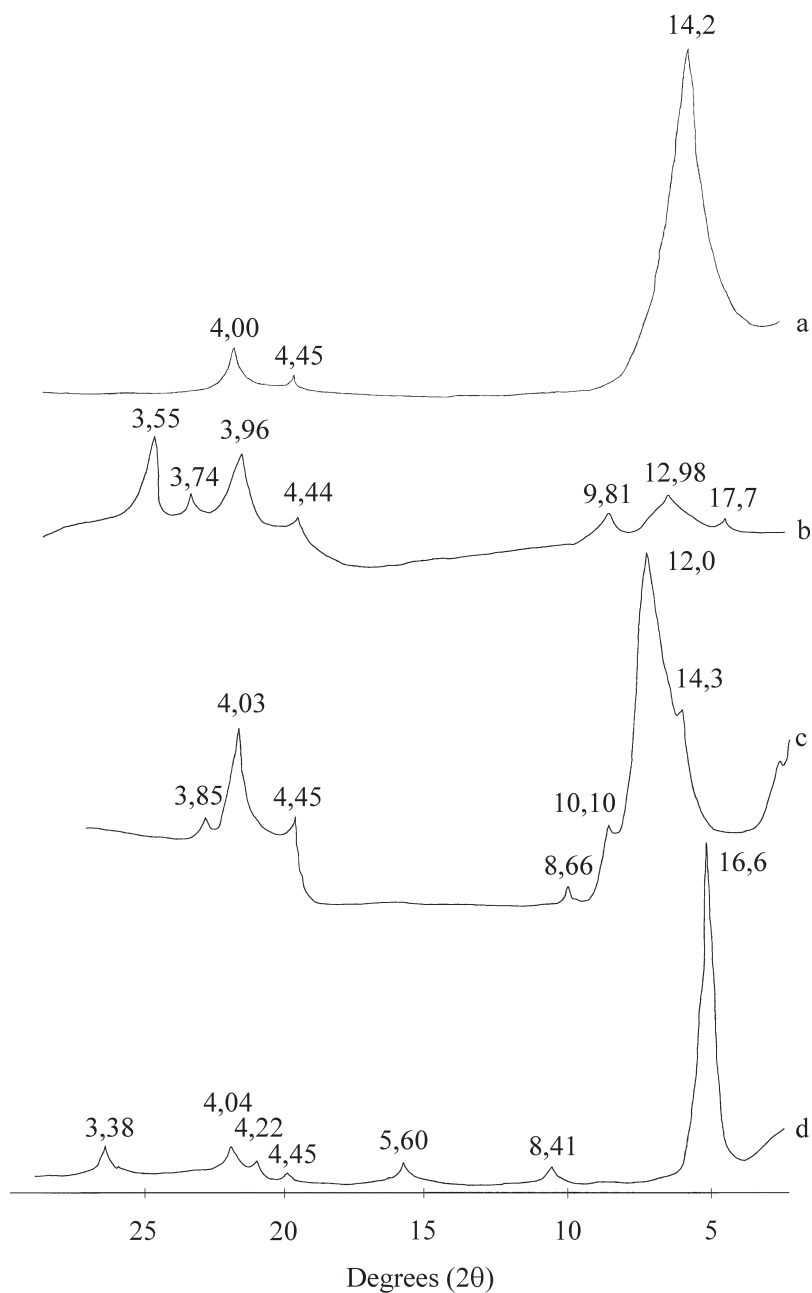
One of serious drawbacks of the Tesla BS-613 electron microscope is that it does not produce 00 $l$  basal reflections from planes parallel to the layers. To acquire 00 $l$  basal reflections, X-ray diffraction traces of  $\text{Pb}(\text{CH}_3\text{COO})_2$ -saturated smectite were produced. As compared to original smectite, X-ray diffraction reflexes for  $\text{Pb}(\text{CH}_3\text{COO})_2$ -saturated smectite were of weak intensity, where 0.981 and 1.298 nm reflexes were clearly identified (Fig. 2). Close spacing values of 0.96 and 1.24 nm for Na-smectite were reported by Moor and Hower (1986), where 0.96 nm corresponded to a dehydrated Na-smectite phase and 1.24 nm corresponded to a hydrated Na-smectite phase with one water molecular. 0.481 nm reflex, which corresponds to 002 reflections of dehydrated interlayer spacing ( $d = 0.96$  nm), was obtained in a dotted electron diffraction pattern of a 'not completely structured fragment' of a crystal and in a circular section of transitional patterns of new-phase crystals with disturbed structure.

X-ray diffraction analysis to clarify structural details of original smectite shows that it may be placed in the category of low-charged smectites, with the charge being predominantly centered in the tetrahedral layer. Smectite saturation with  $\text{K}^+$  results in only insignificant lattice shrinking of a swelling mineral up to 1.0 nm, with the main peak being 1.2 nm. As noted by Weaver (Weaver, 1958), only high-charged smectites show the main peak of 1.0 nm after being saturated with  $\text{K}^+$ . Predominant localization of charge in the tetrahedral layer is proved by Green-Kelly reaction (Green-Kelly, 1953). A 12 h  $300^\circ\text{C}$  heating of a  $\text{Li}^+$ -saturated specimen does not interfere with lattice expansion up to 1.7 nm when the mineral is solvated with ethylene glycol vapour.

Energy of interaction between interlayer cations and smectite layers can be expressed as follows:



**Fig. 1.** TEM images of  $\text{Pb}(\text{CH}_3\text{COO})_2$ -saturated clay minerals. Smectite (a): left – neoformation with a ‘not completely structured’ fragment, right – xenomorphic ‘glued’ conglomerate of smectite crystallites. Kaolinite (b): left – xenomorphic ‘glued’ conglomerate of kaolinite crystallites, arrow – neoformation, (c) – textured aggregate (magnification  $\times 10,000$ ).



**Fig. 2.** X-ray diffraction traces of smectite samples: a - original smectite, b - sample saturated with  $\text{Pb}(\text{CH}_3\text{COO})_2$ , c - sample saturated with  $\text{K}^+$ , d - sample solvated with ethylene glycol vapour after saturation with  $\text{Li}^+$  and heat-treatment at  $300^\circ\text{C}$  for 12 h. The numbers above the peaks are the basal spacings (in angstroms *ie*  $\text{nm}^{-10}$ ).

$$E = \frac{\sigma z e}{2R\epsilon}, \quad (1)$$

where:  $\sigma$  – layer charge density,  $z$  – valence of compensatory cations,  $e$  – electron charge,  $R$  – distance between compensatory cation center and gravity center of macroanion electric charge,  $\epsilon$  – medium dielectric constant. Amongst smectites the energy of interaction between exchange cations and beidellite layers is higher than the one

with montmorillonite layers. As the gravity center of a negative charge is located in tetrahedral cell layer and has  $R$  0.27 nm less as compared to montmorillonite, where negative charge of the cell is mostly centered in its octahedral layer (Tarasevich, 1988). Thus, formation of new-phase crystals, 0.98 nm reflex in X-ray-diffraction traces, charge localization in the tetrahedral layer allow us to assume that smectite saturation with 1N solution of lead



dialysis (Table 1) is nearly twice less as compared to original mineral (12-18 and 50 mg-equiv. 100 g<sup>-1</sup>, respectively) and it also does not exceed illite ability of cation exchange, which is 20 mg-equiv. 100 g<sup>-1</sup>, thus leading to the assumption that after dialysis a certain part of mica-like structure is being preserved. Metastability of inner-sphere 'smectite-Pb<sup>2+</sup>' complex, and hence, instability of new-phase monocrystals with respect to dialysis, is caused by a substantially smaller charge in the layer per elementary cell of smectite and compared to illite (0.2-0.7 (Chukhrov and Smol'yaninova, 1992) and 1.2-1.7 (Gorbunov, 1978), respectively).

identified in Pb(CH<sub>3</sub>COO)<sub>2</sub>-saturated specimens after dialysis.

The appearance of textured aggregates and single neoformation crystals after kaolinite saturation with 1N solution of lead acetate is supposed to be the result of exchange reaction due to formation of inner-sphere cation lead complex with surface functional kaolinite groups. Formation of inner-sphere complex for kaolinite, which is a clay mineral with a rigid structure and zero change in structure layers  $-(T-O)-$ , is impossible theoretically. As illustrated by Chi Ma and Eggleton (1999), this reaction might be attributed to existing surface kaolinite crystals, a 'defect' in

**Table 1.** Composition of exchangeable cations in original minerals and their Pb(CH<sub>3</sub>COO)<sub>2</sub>- and ZnCl<sub>2</sub>- saturated forms, mg-equiv. 100 g<sup>-1</sup> of air-dry mineral

Mineral and saturated salt	Ca	Mg	Na	K	Zn	Pb	Sum
Smectite	<u>20.70</u>	<u>10.63</u>	<u>17.25</u>	<u>1.15</u>	<u>0.09</u>	<u>0</u>	<u>49.82</u>
	24.37	12.37	4.53	2.67	0.08	0.01	44.03
Pb(CH <sub>3</sub> COO) <sub>2</sub>	<u>4.60</u>	<u>3.37</u>	<u>2.48</u>	<u>0.85</u>	<u>0.06</u>	<u>0.15</u>	<u>11.51</u>
	9.76	5.20	1.95	1.00	0.12	0.11	18.14
ZnCl <sub>2</sub>	<u>3.37</u>	<u>1.38</u>	<u>2.39</u>	<u>0.82</u>	<u>21.39</u>	<u>0.08</u>	<u>29.43</u>
	1.73	3.14	4.86	1.06	19.78	0	30.57
Kaolinite	<u>6.59</u>	<u>1.83</u>	<u>1.19</u>	<u>0.13</u>	<u>0</u>	<u>0</u>	<u>9.74</u>
	3.80	1.37	0.48	0.38	0	0	6.03
Pb(CH <sub>3</sub> COO) <sub>2</sub>	<u>0.54</u>	<u>0.85</u>	<u>0.11</u>	<u>0.06</u>	<u>0.06</u>	0.05	<u>1.67</u>
	1.76	1.17	0.26	0.13	0	0.06	3.38
ZnCl <sub>2</sub>	<u>1.14</u>	<u>0.14</u>	<u>0.11</u>	<u>0.06</u>	<u>0.43</u>	<u>0</u>	<u>1.88</u>
	1.08	0.86	0.26	0.13	0.23	0	2.56

Data for saturated and dialyzed forms of minerals are given over and under the line, respectively.

Similar to smectite, Pb(CH<sub>3</sub>COO)<sub>2</sub>-saturated kaolinite electron microscopy revealed 'glued' xenomorphic conglomerations (Fig. 1b, left), all their electron-diffraction patterns were circular. Textured aggregates were also found (Fig. 1c). They showed dotted electron-diffraction patterns. Only single neoformation crystals less than 1 μm in size (Fig. 1b, arrow) were found in Pb(CH<sub>3</sub>COO)<sub>2</sub>-saturated kaolinite. It was impossible to obtain dotted electron-diffraction patterns of neoformation Pb(CH<sub>3</sub>COO)<sub>2</sub>-saturated kaolinite crystals because they were small in size and number. Original kaolinite is represented with conglomerations of hexagonal-shaped electron-nontransparent particles >0.25 μm in size with inclusions of electron-transparent particles with weathered faces (Fig. 1b, right). Neoformation crystals discovered in the experiment are electron-transparent and have distinct unweathered faces. X-ray diffraction traces of Pb(CH<sub>3</sub>COO)<sub>2</sub>-saturated kaolinite, as compared with original ones, were characterized by extremely low reflex intensity, additional reflexes were not registered. Textured aggregates and neoformation monocrystals were not

the ideal kaolinite structure *ie T-O-T* beidellite-type structure, where *T* stands for tetrahedral lattice layers and *O* stands for octahedral ones. Our experimental data for mechanochemical kaolinite behaviour do not disagree with already made conclusions (Chi Ma and Eggleton, 1999) that *T-O-T*-type structures do exist on the surface of kaolinite crystals and that they manifest themselves to the extent to which kaolinite structure is disordered (Kharitonova *et al.*, 2002).

Our analysis revealed that, similar to smectite, the sum of Pb(CH<sub>3</sub>COO)<sub>2</sub>-saturated kaolinite exchange bases is much less than that of original kaolinite and equals to 2 and 10 mg-equiv. 100 g<sup>-1</sup>, respectively. When the absolute value of Pb(CH<sub>3</sub>COO)<sub>2</sub>-saturated kaolinite exchange bases sum sharply drops as compared to kaolinite (from 50 up to 12 mg-equiv. 100 g<sup>-1</sup> and from 10 to 2 mg-equiv. 100 g<sup>-1</sup>, respectively), the relative diminution in exchange cations sums is practically the same as compared to the original minerals. Cation exchange capacity of kaolinite is mostly determined by *T-O-T* structures on the crystal surface (Chi Ma and Eggleton, 1999). The existence on the kaolinite crystal

surface of such structures is imperative for inner-sphere complex formation of Pb<sup>2+</sup> cations with surface functional kaolinite groups. As these elements are not main kaolinite-structure elements, the number of new-phase crystals formed is extremely small, compared to smectite. Bulk X-ray-fluorescent analysis revealed that Pb content in Pb(CH<sub>3</sub>COO)<sub>2</sub>-saturated kaolinite is 98 mg g<sup>-1</sup> and is much less than 222 mg g<sup>-1</sup> for Pb(CH<sub>3</sub>COO)<sub>2</sub>-saturated smectite (Table 2). Besides, structure layers of kaolinite are zero charged, provided that singular surface layer structures 2:1 are excluded. Thus, 'kaolinite-Pb<sup>2+</sup>', inner-sphere complex strength seems negligibly small compared to the one of a respective smectite complex.

Preliminary experiments to study the influence of Zn and Pb salt saturation on smectite and kaolinite sorption characteristics (water vapour sorption) showed its contrary character. ZnCl<sub>2</sub> enhances sorption characteristics of clay

xenomorphic electron-nontransmitting accumulations of 'glued' crystallites. Moreover, multiple mica-like monocystals, hexagonal in shape and up to 3 μm in size, were identified in Pb(CH<sub>3</sub>COO)<sub>2</sub>-saturated smectite.

2. The appearance of neoformations metastable to water may be attributed to inner-sphere complex of Pb<sup>2+</sup> cations and smectite macroanion with its charge being centered in the tetrahedral layer of beidellite structure.

3. Beidellite type of structure serves as obligatory and satisfactory condition for neoformations in Pb<sup>2+</sup> saturated mineral.

4. Textured aggregates and few neoformation monocystals are found in Pb(CH<sub>3</sub>COO)<sub>2</sub>-saturated kaolinite specimens.

5. The methods selected have not made possible any identification of changes in particle organization in clay minerals saturated with 1N ZnCl<sub>2</sub> solution.

**Table 2.** Total Pb<sup>2+</sup> and Zn<sup>2+</sup> in original minerals and their Pb(CH<sub>3</sub>COO)<sub>2</sub>- and ZnCl<sub>2</sub>-saturated forms, mg g<sup>-1</sup> of air-dry mineral

Mineral	Pb		Zn	
	original	Pb(CH <sub>3</sub> COO) <sub>2</sub> -saturated form	original	ZnCl <sub>2</sub> -saturated form
Smectite	0.1	222.0	0.0	34.9
Kaolinite	0.1	98.2	0.0	29.0

minerals and Pb(CH<sub>3</sub>COO)<sub>2</sub> suppresses them (Manucharov *et al.*, 2001). As neoformations and textured aggregates had been discovered after smectite and kaolinite saturation with Pb(CH<sub>3</sub>COO)<sub>2</sub>, ZnCl<sub>2</sub>-saturated minerals were similarly analyzed for comparison purposes. Moreover, as shown previously (Förstner and Wittmann, 1983), Zn<sup>2+</sup> cations can not only sorb in interlayer positions but diffuse into crystal lattice in clay minerals in comparatively unlimited numbers. Data of the second set of experiments showed that neither transmission microphotography (10000-magnification) nor electron microdiffraction and X-ray diffraction of kaolinite and smectite ZnCl<sub>2</sub>-saturated specimens and their dialysis products revealed any changes in particle organization in clay minerals. Bulk X-ray-dispersion analysis indicated that smectite absorbed much less Zn than Pb, 35 and 222 mg g<sup>-1</sup>. These data may indicate the formation in zinc cation outer-sphere complexes with surface functional groups of the minerals studied. Their stability constants are known to be much less than the ones of inner-sphere complexes (Spozito, 1981).

#### CONCLUSIONS

1. Smectite and kaolinite saturation with 1N solution of Pb(CH<sub>3</sub>COO)<sub>2</sub> mostly results in the formation of

#### ACKNOWLEDGMENTS

The authors are grateful to Prof. Dr. T.A. Sokolova from the Moscow State University, Faculty of Soil Sciences for her helpful remarks and advice.

#### REFERENCES

- Chi Ma and Eggleton R.A., 1999.** Surface layer types of kaolinite: a high-resolution transmission electron microscope study. *Clays and Clay Miner.*, 47(2), 181-191.
- Chukhrov F.V. and Smol'yaninova N.N., 1992.** Minerals: A Reference Book. 4(2) (in Russian). Nauka, Moscow.
- Cotton F.A. and Wilkinson G., 1965.** Advanced Inorganic Chemistry. Wiley, New York.
- Förstner U. and Wittmann G.T.W., 1983.** Metal Pollution in the Aquatic Environment. Springer, New York.
- Green-Kelly R., 1953.** Identification of montmorillonites. *J. Soil Sci.*, 4(2), 233-257.
- Gorbunov N.I., 1978.** Mineralogy and Physical Chemistry of Clays (in Russian). Nauka, Moscow.
- Hawkes H. and Webb J., 1962.** Geochemistry in Mineral Exploration. Harper and Row, New York.
- Kharitonova G.V., Zemlyanukhin V.N., Manucharov A.S., and Chernomorchenko N.I., 2002.** Electron-microscopy study of montmorillonite saturated with Pb<sup>2+</sup> and Zn<sup>2+</sup> ions. *Eurasian Soil Sci.*, 35(9), 934-938.

- Kharitonova G.V., Zemlyanukhin V.N., Manucharov A.S., and Chernomorchenko N.I., 2002.** Electron-microscopy study of clay minerals saturated with  $Pb^{2+}$  and  $Zn^{2+}$  ions (in Russian). *Geology of Pacific Ocean*, 21(3), 107-118.
- Manual for Laboratory Methods of Studying the Salt-Ion Composition of Neutral and Alkaline Mineral Soils (in Russian), 1990. The Dokuchaev Institute of Soil Sci., Moscow.
- Manucharov A.S., Kharitonova G.V., Chernomorchenko N.I., and Zemlyanukhin V.N., 2001.** Effect of adsorbed zinc and lead cations on the surface properties of minerals and water vapor sorption. *Eurasian Soil Sci.*, 34(6), 615-620.
- Moor J. and Ramamoorthy S., 1984.** Heavy Metals in Natural Waters: Applied Monitoring and Impact Assessment. Springer, New York.
- Moore D.M. and Hower J., 1986.** Ordered interstratification of dehydrated and hydrated Na-smectite. *Clays and Clay Minerals*, 34(4), 379-384.
- Nekrasov V.V., 1973.** Principles General Chemistry (in Russian). Moscow, 148-193.
- Pinsky D.L., 1997.** Ion-Exchange Processes in Soils (in Russian). Pushino, Russia.
- Savichev A.T. and Sorokin S.E., 2002.** Energy dispersion X-ray fluorescence analysis of macroelements in soil using the reference element technique. *Eurasian Soil Sci.*, 35(12), 1452-1457.
- Spozito G., 1981.** Thermodynamics of Soil Solutions. Oxford University Press.
- Tarasevich Yu.I., 1988.** Structure and Surface Chemistry of Layered Silicates (in Russian). Naukova Dumka, Kiev.
- Weaver Ch.E., 1958.** The effect of geologic significance of potassium 'fixation' by expandable clay minerals derived from muscovite, biotite, chlorite, and volcanic materials. *Amer. Mineral*, 43(9/10), 839-86.