

Sm–Nd Systematics of Fine-Grained Fractions of the Lower Cambrian Blue Clay in Northern Estonia

I. M. Gorokhov, N. N. Mel'nikov, A. B. Kuznetsov,
G. V. Konstantinova, and T. L. Turchenko

*Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences,
nab. Makarova 2, St. Petersburg, 190034 Russia*

e-mail: gorokhov@ig1405.spb.edu

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Abstract—Fine-grained clay subfractions, SFs (particle size <0.1, 0.1–0.4, 0.4–0.6, and 0.6–2.0 μm) separated from a sample of the Lower Cambrian blue clay of the Lontova Formation were studied with XRD and Sm–Nd methods. The relatively coarse-grained SFs include illite with a small admixture of chlorite, while the fine-grained SF (<0.1 μm) consists of mixed-layer illite–smectite. The illite crystallinity index (I_c) increases with decreasing particle size. The leaching of SFs with 1N HCl, analysis of Sm–Nd systematics of leachates and residues, as well as XRD data and results of chemical analysis show that the studied rocks contain at least two generations of minerals. The first (detrital) generation is related to the transformation of provenance material, whereas the second (authigenic) generation was formed at the postsedimentary stage of the evolution of the Lontova sediments. The Sm–Nd date of the first generation (790 ± 90 Ma) is considered a minimal age of rocks in the northeastern and southwestern regions of the East European Platform that served as a source of sedimentary material of the Lower Cambrian blue clay. The date of the second generation of minerals reflects the timing of authigenic mineral formation in the course of burial and diagenetic and catagenetic reworking of clay sediments.

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INTRODUCTION

Unmetamorphosed clastic sedimentary rocks are mixtures of detrital and authigenic minerals that retain isotopic memory about various events in the history of sedimentary material. The age close to the sedimentation time may be obtained only from the earliest authigenic minerals if isotopic-geochemical systems (totality of parental and daughter components in a certain scheme of radioactive decay) of such minerals remain closed at the subsequent stages of lithogenesis. These stages are often marked by the formation of new authigenic minerals or the transformation of older minerals. The response of Sm–Nd, Rb–Sr, and K–Ar isotopic systems to the change of geochemical environment is determined by chemical properties of their components. Therefore, various isotopic-geochronological methods used for analysis of the same sedimentary materials may yield different age estimates that correspond to different stages of lithogenesis. Thus, based on combination of the analyzed materials and methods, one can obtain more comprehensive information concerning the geological and geochemical history of clastic sedimentary rocks.

The practice of geochronological research has shown that division of the common (<2 μm) clay fraction of mudstone into several size SFs is the best way to obtain the material suitable for the isotopic dating of

lithogenetic processes (Morton, 1985a; Clauer et al., 1990; Bros et al., 1992; Gorokhov et al., 1994, 1997, 2001a, 2002; Schaltegger et al., 1994; Grathoff et al., 1998, 2001; Zwingmann et al., 1999). In general, such SFs represent mineral mixtures. However, the end members of these mixtures, which are composed of noncogenetic generations of individual minerals, commonly predominate in the coarsest and finest SFs (Gorokhov et al., 1997, 2001b, 2002, 2006; Grathoff et al., 1998, 2001). The clay component in the SF is identified by the XRD analysis and the determination of illite polytype and crystallinity index (Kubler, 1966, 1990; Pevear, 1992; Grathoff and Moore, 1996, 2002; Meunier and Velde, 2004). The method of leaching with hydrochloric acid or ammonium acetate solutions and the subsequent isochron analysis are used to date each SF with the Rb–Sr method (Clauer et al., 1990, 1993; Gorokhov et al., 1994; Ohr et al., 1994; Clauer and Chaudhuri, 1995).

New perspectives for the study of such SFs have been demonstrated in many publications (Mossmann, 1991; Bros et al., 1992; Schaltegger et al., 1994; Grathoff et al., 1998, 2001; Gorokhov et al., 2001b, 2002, 2005, 2006). They showed that various clayey rocks (soaking clays, mudstones, and shales) may contain several generations of authigenic minerals formed at different stages of lithogenesis. We attempted to utilize this phenomenon for the Sm–Nd dating of different

stages in the geological history of ancient sedimentary rocks.

The abundance of REE in whole-rock samples of mudstones is actively studied to identify sedimentary material sources. It is often assumed that REEs remain relatively immobile in clayey rocks and do not fractionate in the course of catagenesis (Cullers et al., 1975; Chaudhuri and Cullers, 1979; Clauer et al., 1990). However, based on the study of Phanerozoic mudstones of the Greater Caucasus and East European Platform, Balashov and Girin (1969) made the following conclusions: (1) the sedimentary rocks contain a sufficient amount of REEs that can migrate in the process of diagenesis and catagenesis; (2) if the clay fraction is treated with hydrochloric acid or ammonium oxalate, the solution tends to be enriched in MREE and HREE, whereas the clay residue is enriched in LREE. The tendency of LREE accumulation in authigenic clay minerals and the enrichment of diagenetic fluids (hence, precipitated cement) in MREE was corroborated in several works (Mack and Awwiller, 1990; Awwiller and Mack, 1991; Ohr et al., 1991, 1994; and Awwiller, 1994). Significant difference in the Sm/Nd ratio of acid-soluble and insoluble components of mudstones suggested that the Sm-Nd isotopic system of mudstones may be utilized to determine their age if these components were in isotopic equilibrium at certain stages of lithogenesis (Ohr et al., 1991, 1994; Bros et al., 1992; Awwiller, 1994).

The objective of the present work was to estimate the scope of the Sm-Nd method for studying the Lower Cambrian blue clay of the Lontova Formation (northern Estonia). Numerous Rb-Sr and K-Ar data on the Lontova clay are reported in (Polkanov and Gerling, 1960; Firsov et al., 1971; Krasnobaev et al., 1986; Clauer et al., 1993, 2003; Gorokhov et al., 1994, 1995; Chaudhuri et al., 1999; Kirsimäe et al., 1999a). We attempted to elucidate the following issues: (1) the ranges of Sm and Nd concentrations in silicate (clay) and acid-soluble (mobile) components of the fine-grained SFs of blue clays, (2) the Sm-Nd systematics of mixing for the clay and mobile components, and (3) preliminary assessment of the suitability of the XRD and Sm-Nd analysis of varisized SFs for the dating of geological events responsible for the formation of clastic and authigenic minerals in ancient clayey rocks.

GEOLOGY

The pre-Late Vendian peneplain, which marks the pre-Phanerozoic ground surface, has been retained well beneath the sedimentary cover in Estonia. The total thickness of the now existing Phanerozoic sedimentary rocks does not exceed 800 m. 500–800 m of Phanerozoic sediments could be eroded. The Lower Paleozoic section of Estonia comprises three sequences: the Vendian–Tremadocian sequence of mainly terrigenous rocks, the Ordovician–Silurian carbonate sequence, and the Devonian terrigenous rocks. The thickness of

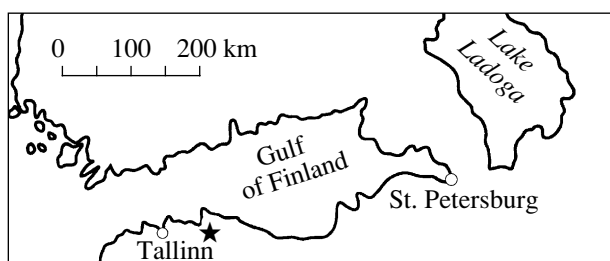


Fig. 1. Index map. Location of the study sample is shown by asterisk.

the lower (Vendian–Tremadocian) sequence locally reaches 220 m. Hiatuses in this sequence were related to transgressions and regressions in the tectonic evolution of the East European Platform (*Geology...*, 1997).

The Cambrian sedimentary rocks of northern Estonia are divided into three formations (from bottom to top): the Lontova Formation (blue clays), the Lukati Formation, and the Tiskre Formation (Mens and Pirrus, 1977). The Lower Cambrian Lontova Formation, which contains diverse fossils (sabellidites, platysolenites, brachiopods, acritarchs, and others), is largely composed of marine hydromicaceous clays. Interlayers of sandstones and less frequent siltstones occur only in the lower part of this formation. The upper section of the Lontova Formation is exposed in open pits and at cliffs on the southern coast of the Gulf of Finland.

Lower Cambrian sediments of northern Estonia were probably deposited under normal marine conditions (Mens and Pirrus, 1986) in a relatively shallow-water epicontinental basin of the Baltica continent. In the Late Precambrian and Early Paleozoic, the continent was located at high and moderate southern latitudes and separated from northern Gondwana and Laurentia by the Tornquist Sea and Iapetus Ocean, respectively (Torsvik et al., 1992). A significant amount of clayey sediments was deposited in the Lontova time over the entire East European Platform.

Blue clays of northern Estonia represent a unique complex of the unmetamorphosed Lower Cambrian clayey sediments that retained plasticity and soaking property. Judging from the preservation degree of organic matter of microfossils, these rocks were never heated above 50°C and the maximum depth of subsidence was not greater than 800–1000 m (Kirsimäe et al., 1999b). Nevertheless, the study with Rb-Sr and K-Ar methods has shown that the blue clays contain at least two or more noncogenetic generations of clay minerals, including authigenic varieties (Gorokhov et al., 1994; Kirsimäe et al., 1999a; Chaudhuri et al., 1999). Sample 807/6 of blue clays was taken in the Kolgakula open pit near the town of Loksa (northern Estonia) from the upper (Kestla) member of the Lower Cambrian Lontova Formation (Fig. 1).

Table 1. Mineral composition of the clay subfractions

Subfraction, μm	Chlorite, %	Illite, %	Illite crystallinity index, I_c
1–2	15	85	0.26
0.4–0.6	15	85	0.26
0.1–0.4	10	90	0.50
<0.1	–	100	1.51

METHOD

The sample was carefully ground by a hand-power press and multifold sieving of fraction <0.25 mm. Further, fraction <2 μm was separated by routine sedimentation in distilled water and divided by centrifuging into size SFs with the particle size of <0.1, 0.1–0.4, 0.4–0.6, and 0.6–2.0 μm .

The mineral composition of clay material and illite crystallinity index I_c (Kubler, 1966) were determined by the XRD method. The oriented SF slides with an approximately constant thickness of layer were used for obtaining three X-ray patterns of the following preparations: (1) untreated SF, (2) SF saturated with ethylene glycol vapor for 12 h, and (3) SF heated in air for 4 h at 490°C (Clauer et al., 1997). The I_c value obtained corresponds to the width of 10 Å (001) peak of illite in angular degrees (Kisch, 1980) measured at its half-height.

All SFs were leached with 1N HCl at room temperature. The charge of leachable SF varied from 60 to 100 mg depending on the amount of the available substance. The leachate and residue were separated by centrifuging. The residue was twice washed with bidistilled water, and the washing water was added to the leachate. The leachates, residues, and untreated SFs were analyzed with the Sm–Nd method. In addition, concentrations of the major, minor, and rare earth (REE) elements were determined in leachates with the ICP-AES and ICP-MS methods with an uncertainty of about $\pm 10\%$ (1σ).

For the Sm–Nd isotopic analysis, a solution of mixed ^{149}Sm – ^{150}Nd spike was added to the analyzed specimen, and the clay matter was decomposed by the ($\text{HCl} + \text{HNO}_3 + \text{HF} + \text{HClO}_4$) mixture at a temperature of 105°C. After evaporation, the residue was treated by the concentrated ($\text{HCl} + \text{HNO}_3$) mixture with heating. The evaporated residue was dissolved in 2.4N HCl and passed through an ion-exchange column (6 $\times$ 110 mm) filled with Dowex AG 50W $\times$ 8 resin (200–400 mesh). This procedure was also applied for the leachate. The REE-bearing fraction was picked in the course of elution with 4N HCl. The precipitate left after evaporation was dissolved in 0.1N HCl and introduced into an ion-exchange column (7 $\times$ 50 mm) filled with an LN-C50-A resin, 100–150 mesh (Elchrom Company). Nd and Sm were separated by elution with 0.3N and 0.7N HCl, respectively.

The Sm and Nd isotopic compositions were measured on a Finnigan MAT 261 multicollector mass spectrometer in static mode. The Nd isotope ratios were normalized to the $^{146}\text{Nd}/^{144}\text{Nd}$ ratio of 0.7219. During the period of data gathering, the average $^{143}\text{Nd}/^{144}\text{Nd}$ value was 0.511857 ± 0.000010 ($2\sigma_{\text{mean}}$, $n = 7$) for the La Jolla standard and 0.512105 ± 0.000009 ($2\sigma_{\text{mean}}$, $n = 18$) for the JNdi-1 standard normalized to $^{148}\text{Nd}/^{144}\text{Nd} = 0.241578$. The procedure blank was 0.05 ng for Sm and 0.2 ng for Nd. The analytical uncertainty in samples was accepted at $\pm 0.5\%$ for $^{147}\text{Sm}/^{144}\text{Nd}$ and $\pm 0.005\%$ for $^{143}\text{Nd}/^{144}\text{Nd}$. Uncertainties in the text and plots presented in this paper are quoted at the 2σ level. During the period of data gathering, the average Sm and Nd contents in the BCR-1 standard sample were 6.53 and 28.58 $\mu\text{g} \cdot \text{g}^{-1}$, respectively. The decay constant $^{147}\text{Sm} = 6.54 \times 10^{-12} \text{ yr}^{-1}$ was used to calculate ages. The $\epsilon_{\text{Nd}}(t)$ and $t_{\text{Nd}}(\text{DM})$ values were calculated on the basis of the following values: $^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$ and $^{147}\text{Sm}/^{144}\text{Nd} = 0.1967$ for CHUR (Jacobsen and Wasserburg, 1984); $^{143}\text{Nd}/^{144}\text{Nd} = 0.513151$ and $^{147}\text{Sm}/^{144}\text{Nd} = 0.2136$ for DM (Goldstein and Jacobsen, 1988).

RESULTS

Mineralogy. The weight percentages of SFs of particle sizes 0.6–2.0, 0.4–0.6, 0.1–0.4, and <0.1 μm in fraction <2 μm are 4, 7, 57, and 32%, respectively. The relatively coarse-grained SFs (0.6–2.0, 0.4–0.6, and 0.1–0.4 μm) are composed of illite (80–90%) with some amount of expandable layers and chlorite (10–20%). The fine-grained SF (<0.1 μm) consists of only mixed-layer illite–smectite. The I_c parameter varies from values typical of the anchimetamorphism zone in SF 0.6–2.0 μm to values typical of dia- and catagenetic zones in the fine-grained SF (Table 1). Thus, illite polytype $2M_1$ plays a significant role in the coarse-grained SFs, whereas the low-temperature polytypes $1M$ and $1M_d$ predominate in the fine-grained SFs (Gorokhov et al., 1994; Kirsimäe et al, 1999a). Results of the TEM analysis of other samples of the Lontova blue clay reported in (Gorokhov et al., 1994, 1995) revealed the following regularity: illite crystals have a typically detrital appearance in the coarse-grained SF (0.6–2.0 μm); the growth of authigenic lath-shaped illite crystals is observed in the medium-grained SFs; and only lath-shaped crystals occur in the fine-grained SF (<0.1 μm). Thus, the XRD and morphological data clearly indicate that the silicate material of the Lontova clay is a mixture of noncogenetic mineral generations.

Chemical composition of leachates. Tables 2 and 3 present contents of the major, minor, and rare earth elements in leachates from varisized SFs determined with the ICP method. The chemical composition of leachates is of interest, because it may bear information on minerals completely or partly dissolved in the pro-

cess of laboratory leaching. The leaching with acid and ammonium salt solutions results in the extraction of Sm, Nd, Sr, Rb, and other elements from the nonsilicate material and exchangeable interlayer sites in the lattice of clay minerals (Ohr et al., 1991, 1994; Bros et al., 1992; Schaltegger et al., 1994; Gorokhov et al., 1994, 1997, 2001a, 2001b, 2002, 2005; Clauer and Chaudhuri, 1995). However, this process is not probably accompanied by any preferential removal of radiogenic isotopes (Clauer et al., 1993). The HCl-soluble nonsilicate material of clayey and silty rocks is commonly represented by three components: the carbonate and phosphate accessory minerals formed at various stages of lithogenesis and the hydroxide shells of mineral grains.

Muriatic leachates from sample 807/6 mainly include K, Ca, Al, Fe, and Mg. A similar composition of leachate was established for the Cambrian mudstones from northwestern Morocco (Schaltegger et al., 1994). Na, Sr, Ba, P, Mn, and REE are subordinate, while Y, Cu, Ni, Ti, Zr, B, Pb, and Sc occur as trace elements. K, Ca, Al, Fe, Mg, Na, Mn, Ba, Sr, Ni, Zr, B, and Sc concentrations in leachates show a negative correlation with the clay particle size. Increase in Sr, K, Mg, and Ca concentrations from coarse-grained to fine-grained SFs is 7.2, 6.5, 5.5, and 4.1 times, respectively. Increase in Al, Ba, Na, Mn, and Fe concentrations is moderate (1.6–3.1 times). P and Ti show a positive correlation.

High concentrations of Ca, Mg, and Fe may be explained by the dissolution or leaching of ankerite microinclusions. Correlation between Fe and Mg in leachates after the dissolution of chlorite is less probable because of the absence of this mineral in the finest SF, the leachate from which contains abundant Fe and Mg. Oxides and hydroxides may be another source of Fe in blue clays. A more significant increase in Mg and Ca contents relative to Mn and Fe in the finest SF (<0.1 μm) can be caused by increase in the share of the carbonate phase relative to the hydroxide phase. High K and Al concentrations likely reflect the transition of aluminosilicate phase(s) into solution. Let us note that the K/Al ratio in leachates depends on the size of clay particles: two times higher in the fine-grained SF (<0.1 μm) relative to the coarse-grained SFs (0.4–0.6 and 0.6–2.0 μm). It is rather difficult to explain the origin of high K concentrations, because the content of K-feldspar in the SFs is negligible and this element cannot be easily removed from interlayer sites in mica by means of diluted acids. Therefore, we are forced to assume that the finest SF contains a relatively soluble micaceous component.

The size of clay particles in the SFs shows a positive correlation with REE concentration in leachates (Table 3, Fig. 2). In the leachate of SF <0.1 μm , the REE concentration is appreciably lower than in the leachate of the coarser SFs. Tables 3 and 4 allow us to compare the Sm and Nd contents determined by the ICP-MS analysis

Table 2. Concentrations of the major and minor elements, $\mu\text{g/g}$ in muriatic leachates from the clay subfractions (ICP-AES data)

Element	Size subfraction, μm			
	<0.1	0.1–0.4	0.4–0.6	0.6–2.0
Al	1900	1420	910	600
Fe	1310	1500	1330	800
Mg	1390	960	475	250
Ca	3210	2280	1340	780
Na	48	34	33	23
K	1660	960	400	260
Mn	17	17	12	8.1
Ba	50	34	25	18
Sr	50	31	13	6.8
Ti	1.3	2.0	2.0	2.6
P	51	178	178	120
Cu	4.2	2.4	3.6	7.9
Pb	1.4	2.8	3.6	2.0
Ni	3.9	2.6	1.5	2.1
Zr	3.8	2.3	1.2	0.8
B	2.6	2.0	0.8	0.6
Sc	0.9	0.5	0.2	0.1
Y	2.8	6.2	7.5	4.5

Note: Concentrations in leachates are recalculated to 1 g of the untreated subfraction.

Table 3. REE concentrations, $\mu\text{g/g}$ in leachates from the fine-grained subfractions (ICP-MS data)

Element	Size subfraction, μm			
	<0.1	0.1–0.4	0.4–0.6	0.6–2.0
La	3.8	5.8	5.0	4.2
Ce	11.5	18.4	17.9	14.0
Pr	1.6	2.5	2.5	1.9
Nd	6.5	11.9	12.4	9.1
Sm	1.3	2.9	3.3	2.3
Eu	0.26	0.59	0.69	0.47
Gd	1.1	2.7	3.2	2.2
Tb	0.13	0.34	0.41	0.28
Dy	0.59	1.58	1.90	1.32
Ho	0.09	0.24	0.29	0.20
Er	0.21	0.53	0.62	0.43
Tm	0.026	0.063	0.072	0.051
Yb	0.14	0.32	0.37	0.26
Lu	0.020	0.044	0.048	0.035

Note: Concentrations in leachates are recalculated to 1 g of the untreated subfraction.

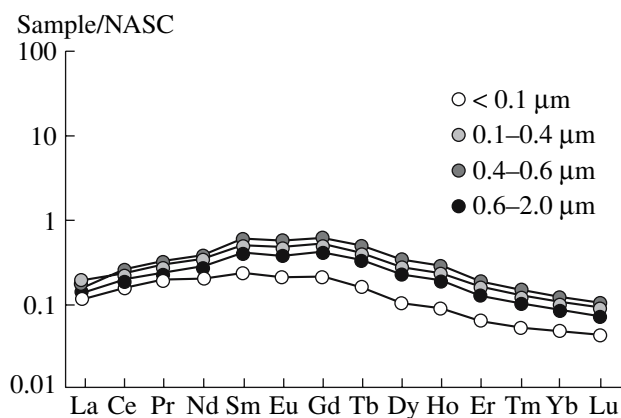


Fig. 2. NASC-normalized REE patterns in leachates.

and the mass-spectrometric method of isotopic dilution. One can see that these results are comparable within the limits of analytical uncertainties except for SF 0.6–2.0 μm .

Relative shares of Sm and Nd, which pass into the leachate, increase with decrease in particle size from 30.6 to 39.6% for Sm and from 21.3 to 32.5% for Nd (Fig. 3a). Similar proportions of the leached REE were obtained for the Lontova clay by Clauer et al. (1993) who also used 1N HCl for the leaching. This technique is well reproducible: in three duplicate analyses for each fine-grained SF (0.1–0.4 and <0.1 μm), the relative share of the leached material ranges from 36.4 to 38.5% and from 37.8 to 39.6%, respectively, for Sm and from 25.7 to 27.4% and from 31.3 to 32.5%, respectively, for Nd (Table 4). The balance of materials in these runs was not worse than $\pm 3\%$, testifying to analytical correctness of the leaching procedure.

The chemical composition of leachates suggests that the major part of REE (including Sm and Nd) transferred into solution was contained in soluble accessory minerals rather than in exchangeable sites of the crystal structure of clay minerals. The positive correlation of LREE concentrations (from La to Sm) and P in leachates (Table 2, Fig. 4a) casts no doubt that apatite is an important carrier of REE in the Lontova blue clay. The REE concentration in apatite is very high (1000–3000 $\mu\text{g/g}$ Nd). Therefore, even small amounts of this mineral can provide significant contents of these elements in leachates. Amorphous iron hydroxide shells of mineral grains contain relatively lower but still substantial REE concentrations (~ 150 – 600 $\mu\text{g/g}$ Nd) (Elderfield et al., 1981; Palmer, 1985). Therefore, some part of REE in the Lontova clay could be adsorbed by iron oxyhydroxides at the stage of sedimentation. However, the absence of Ce anomaly in REE patterns of leachates (Fig. 2) is contradictory to this assumption. At the same time, the negative correlation Ca and P (Fig. 4b) indicates that decrease in the SF particle size is accompanied by enrichment in the P-free but Ca-rich accessory mineral (ankerite or another carbonate). This sugges-

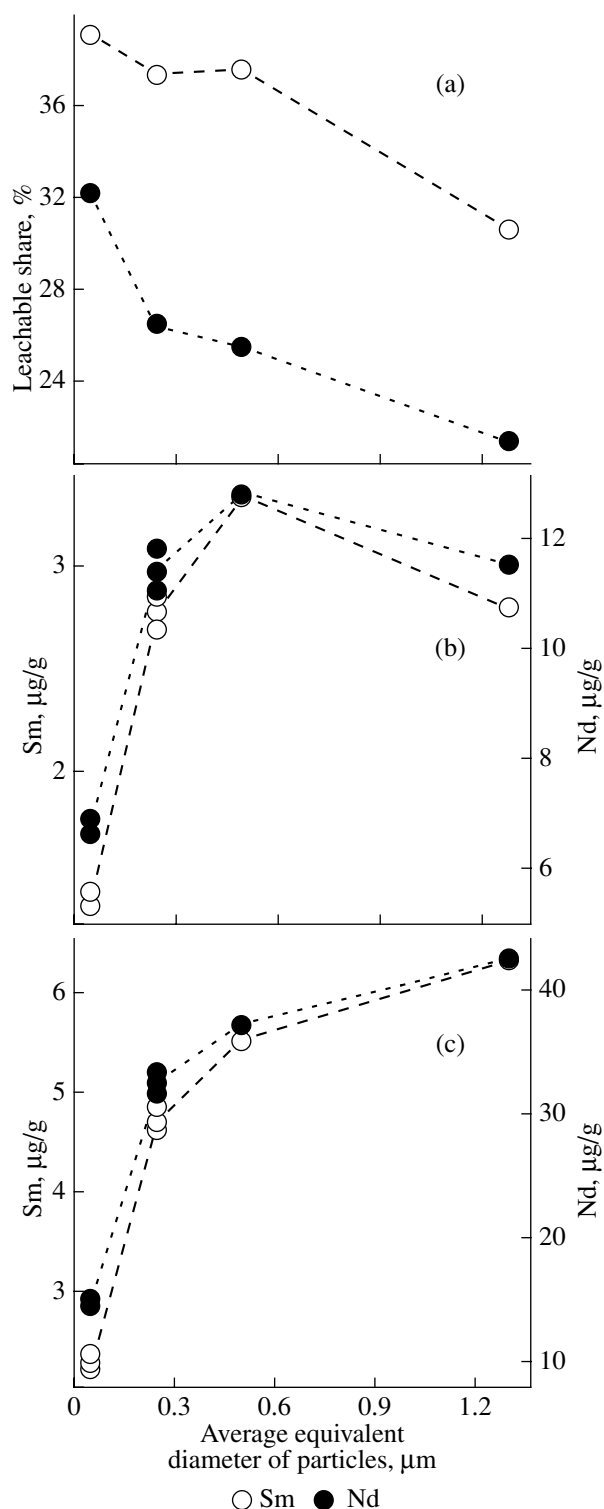


Fig. 3. Composition of leaching products of varisized sub-fractions: (a) Sm and Nd shares leached with 1N HCl; (b) Sm and Nd concentrations in leachate; (c) Sm and Nd concentrations in residue.

tion is corroborated by the depletion of leachates in REEs with the decrease in the SF particle size, because REE contents are very low in many carbonates. Thus, the composition of leachates, which can probably con-

Table 4. Analytical Sm–Nd data on the fine-grained subfractions

Particle size, μm	Specimen	Share transferred into leachate, %		Sm, $\mu\text{g/g}$	Nd, $\mu\text{g/g}$	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	Balance, %	
		Sm	Nd					Sm	Nd
0.6–2	U	30.6	21.3	9.13	54.3	0.1018	0.511922	0.0	0.0
	L			2.80	11.5	0.1465	0.512149		
	R			6.34	42.8	0.0896	0.511852		
0.4–0.6	U	37.6	25.5	8.89	50.5	0.1063	0.511958	–0.3	–0.4
	L			3.34	12.9	0.1570	0.512196		
	R			5.52	37.5	0.0890	0.511851		
0.1–0.4	U			7.44	43.4	0.1035	0.511903		
	U			7.39	43.1	0.1036	0.511900		
	L ₁	38.5	27.4	2.86	11.9	0.1457	0.512118	+2.0	+2.9
	R ₁			4.71	32.7	0.0871	0.511855		
	L ₂	37.4	26.4	2.77	11.4	0.1466	0.512108	–0.2	+0.2
	R ₂			4.62	31.9	0.0876	0.511873		
	L ₃	36.4	25.7	2.70	11.1	0.1466	0.512083	+2.0	+2.7
	R ₃			4.87	33.4	0.0883	0.511852		
<0.1	U			3.58	21.2	0.1020	0.511938		
	U			3.59	21.3	0.1021	0.511945		
	L ₁	39.6	32.4	1.42	6.89	0.1246	0.512018	+1.7	+1.6
	R ₁			2.22	14.7	0.0915	0.511887		
	L ₂	39.5	32.5	1.41	6.91	0.1238	0.512019	+2.9	+2.8
	R ₂			2.27	14.9	0.0921	0.511894		
	L ₃	37.8	31.3	1.35	6.65	0.1232	0.511997	+3.0	+2.8
	R ₃			2.34	15.2	0.0930	0.511903		

Note: (U) Subfraction untreated with 1N HCl; (L) leachate; (R) residue. Subscripts designate run numbers. Sm and Nd concentrations in leachates are recalculated to 1 g of the untreated SF.

tain an insignificant amount of desorbed components of pore fluid, is largely determined by the presence of dissolved microinclusions of phosphate and carbonate minerals.

The NASC-normalized (Gromet et al., 1984; Condie, 1991) REE pattern in SF 0.6–2.0 μm of the Lontova clay demonstrates a gradual enrichment in LREE, and the $(\text{La}/\text{Yb})_n$ ratio is close to 2 (Clauer et al., 1993). The medium-grained SF (<0.4 μm) is also enriched (but to a lesser extent) in LREE. This enrichment pattern of clayey material is retained after the SF treatment with 1N HCl. The most appreciable growth of concentrations in both SFs is noted at the transition from Tb and Eu to Sm and Nd (Clauer et al., 1993). At the same time, the distinctly hump-shaped NASC-normalized REE patterns in leachates from sample 807/6 (Fig. 2) implies that the material removed by HCl from all clayey SFs is enriched in MREE (from Sm to Tb). A

similar REE pattern of leachates from the unmetamorphosed Phanerozoic clayey rocks was pointed out by many authors (Clauer et al., 1993, 1997; Schaltegger et al., 1994; Awwiller, 1994; Zwingmann et al., 1999). However, the nature of this phenomenon remains unclear and controversial.

Most researchers suggest that enrichment of the leachates in MREE is a consequence of the catagenetic illitization of smectites and the mixed-layer illite-smectites as well as the authigenic phosphate formation. Although the mechanism of illitization has remained a debatable issue for many years (Hower et al., 1976; Boles and Franks, 1979; Morton, 1985b; Eberl, 1993; Meunier and Velde, 2004), illitization of smectite is commonly attributed to progressive recrystallization during the burial of sediments until the exhaustion of potassium available in the environment. REEs could fractionate in the process of recrystalliza-

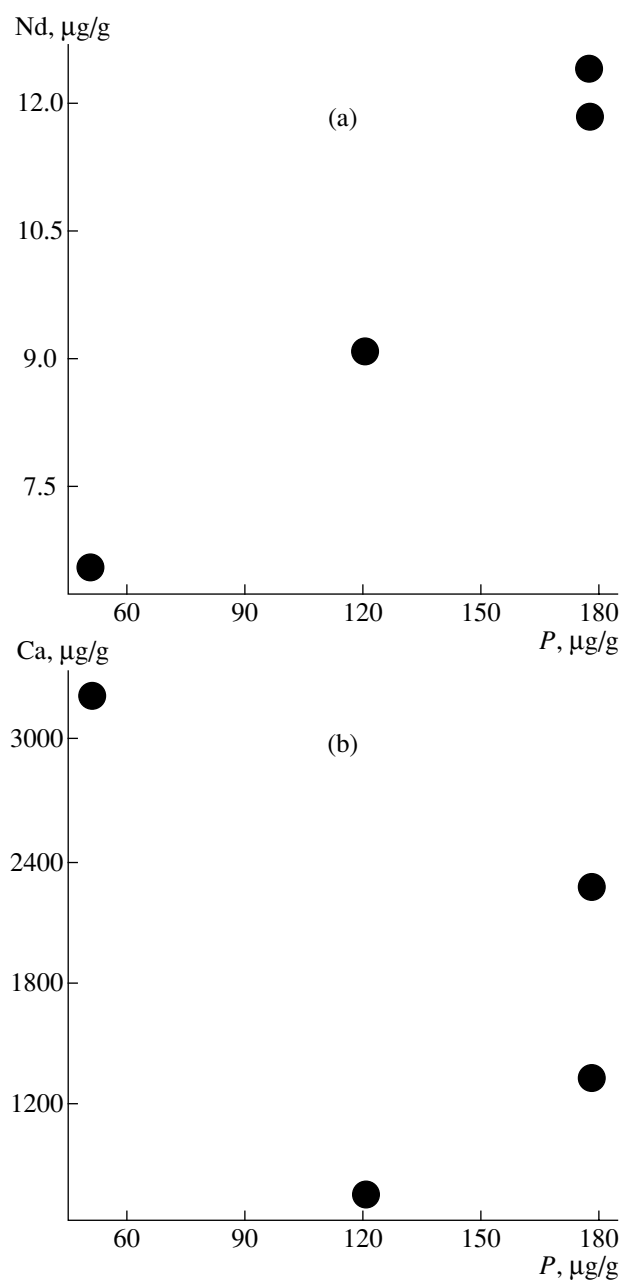


Fig. 4. Correlation of (a) Nd and (b) Ca with P in leachates from varisized subfractions.

tion. In theory, REEs can occupy two sites in the crystal structure of illite–smectite (Awwiller, 1994): (i) within interlayer sites along with K and (ii) in octahedral layers together with Mg, Fe, and Al. Ionic radius of the trivalent LREEs in interlayer sites is close to the ionic radius of Na^+ (Shannon, 1976), which commonly replaces a small amount of K^+ in illite. Thus, the illite–smectite interlayer sites (if they somehow discriminate cations at all) should largely be replaced by LREEs. The octahedral layers should display the trend of HREE prevalence, because Yb^{3+} is closest (in size) to the typical octahedral cations (Mg^{2+} , Fe^{2+} , Fe^{3+} , and Al^{3+}).

However, the radius of this ion is larger by 0.1 Å relative to Fe^{2+} , the largest member among the common cations in the octahedral layer. Therefore, REEs should not enter the octahedral sites as easily as the interlayer sites (Awwiller, 1994).

The REE concentration in apatite can be one to two orders of magnitude higher than in the NASC (Młodowski and Zalasiewicz, 1991), especially as concerns the MREE. In the crystal structure of apatite, REEs probably replace Ca^{2+} (ionic radius 1.12 Å). Such a replacement should be easy for Nd^{3+} and Sm^{3+} owing to the closeness of their ionic radii (1.11 Å and 1.08 Å, respectively, for the eightfold coordination) (Wright et al., 1987). However, discrepancy between the charge and radius does constrain the incorporation of REEs into apatite. Nevertheless, the pre-Jurassic and younger phosphates often demonstrate hump-shaped REE patterns (Wright et al., 1984, 1987; Grandjean et al., 1987; Grandjean and Albarède, 1989; Grandjean–Lécuyer et al., 1993; Kidder and Eddy-Dilek, 1994; Holser 1997; Reynard et al., 1999; Bouch et al., 2002; Kidder et al., 2003). Thus, the dia- and catagenetic precipitation of phosphates also may induce the fractionation of REEs with the enrichment in MREE. Leachates from clayey rocks appear to this enrichment pattern in apatite microinclusions.

Sm–Nd systematics of mixing in leachates and residues. Like other REEs, Sm and Nd concentrations in leachates from the coarse-grained SFs (from 0.6–2.0 to 0.1–0.4 µm) show minor variations from 2.8 to 3.3 and from 11.5 to 12.9 µg/g, respectively (Table 4; Fig. 3b), but they abruptly fall to 1.4 µg/g (Sm) and 6.8 µg/g (Nd) in SF < 0.1 µm. In contrast, in residues (Fig. 3c), the contents decrease gradually from 6.3 to 2.3 µg/g (Sm) and from 42.8 to 14.9 µg/g (Nd) with decrease in the particle size from 0.6–2.0 to < 0.1 µm.

The $^{147}\text{Sm}/^{144}\text{Nd}$ ratio in leaching products is highly variable. It varies from 0.123 (fine-grained SFs) to 0.157 in leachates (Fig. 5a) and from 0.087 to 0.093 in residues (Fig. 5c). The $^{143}\text{Nd}/^{144}\text{Nd}$ values in these components of varisized SFs fall into intervals 0.511997–0.512196 and 0.511851–0.511903, respectively. The low Sm/Nd ratio in the silicate material is typical of illite (Awwiller and Mack, 1991; Ohr et al., 1991, 1994; Bros et al., 1992; Awwiller, 1994; Schaltegger et al., 1994). High Sm/Nd and $^{143}\text{Nd}/^{144}\text{Nd}$ values in the leachates likely characterize the dissolved phosphate mineral(s) enriched in REE in the coarse-grained SFs, whereas lower ratios in the fine-grained SFs should be ascribed to the carbonate component of the Lontova clay.

DISCUSSION

Let us take a mixture of two components 1 and 2. Suppose that atomic concentrations of ^{147}Sm , ^{143}Nd , and ^{144}Nd are $^{147}\text{Sm}_1$, $^{143}\text{Nd}_1$, $^{144}\text{Nd}_1$ and $^{147}\text{Sm}_2$,

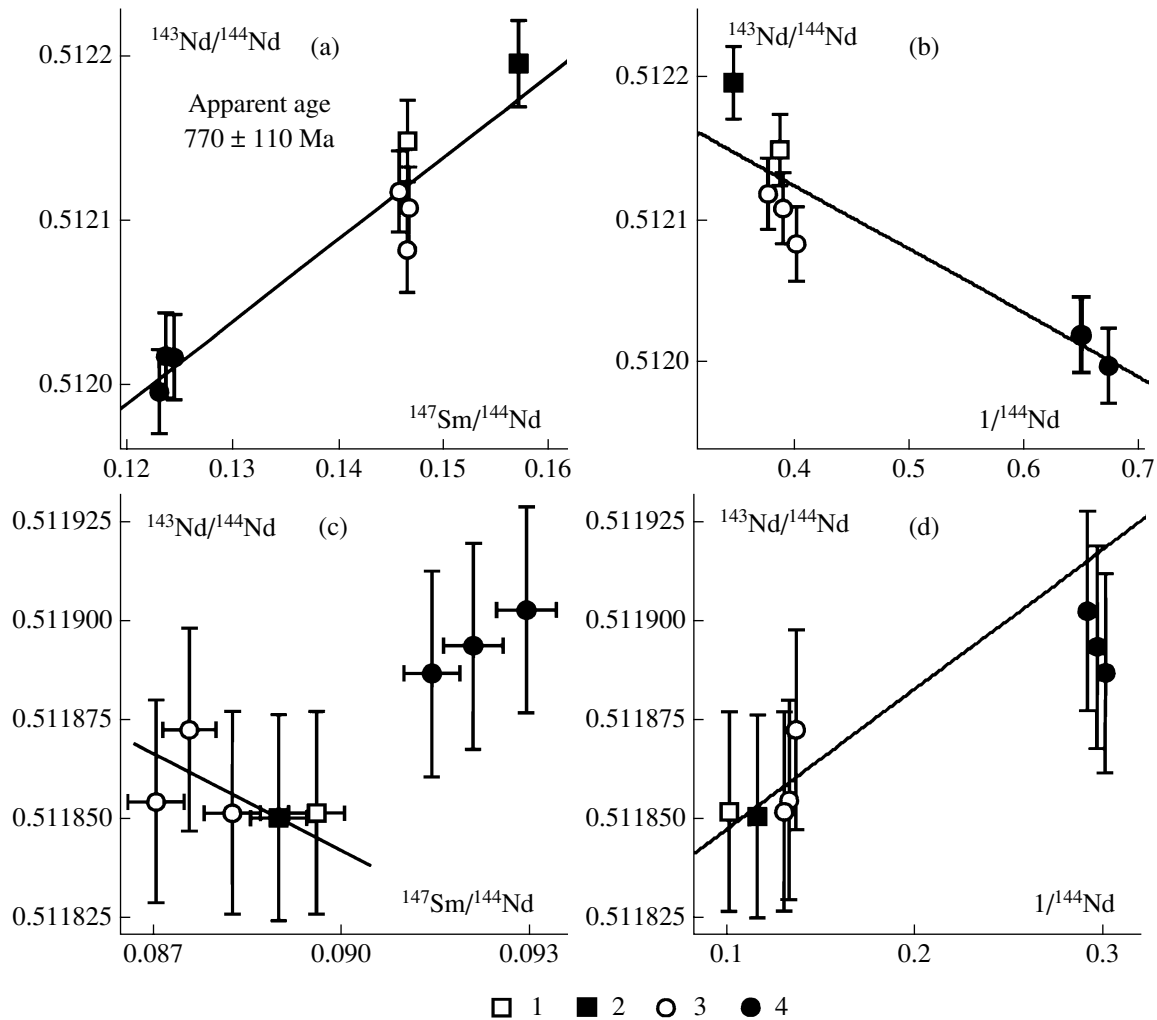


Fig. 5. Isotopic compositions of leaching products of varized subfractions plotted on mixing diagrams in coordinates $^{147}\text{Sm}/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ and $1/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$: (a, b) leachate, (c, d) residue; (1–4) subfractions, μm : (1) 0.6–2.0, (2) 0.4–0.6, (3) 0.1–0.4, (4) <0.1.

$^{143}\text{Nd}_2$, $^{144}\text{Nd}_2$, respectively, in these components and $^{147}\text{Sm}_m$, $^{143}\text{Nd}_m$, $^{144}\text{Nd}_m$, respectively, in their mixture.

Then, the equation of mixing line in the $^{147}\text{Sm}/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ plot is as follows:

$$\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_m = \frac{(^{147}\text{Sm}/^{144}\text{Nd})_2(^{143}\text{Nd}/^{144}\text{Nd})_1 - (^{147}\text{Sm}/^{144}\text{Nd})_1(^{143}\text{Nd}/^{144}\text{Nd})_2}{(^{147}\text{Sm}/^{144}\text{Nd})_2 - (^{147}\text{Sm}/^{144}\text{Nd})_1} + \frac{(^{143}\text{Nd}/^{144}\text{Nd})_2 - (^{143}\text{Nd}/^{144}\text{Nd})_1}{(^{147}\text{Sm}/^{144}\text{Nd})_2 - (^{147}\text{Sm}/^{144}\text{Nd})_1} \left(\frac{^{147}\text{Sm}}{^{144}\text{Nd}}\right)_m \quad (1)$$

which represents a straight line of type $Y = a + bX$. Thus, data points of components 1 and 2 mixed in different proportions should lie in the specified coordinates along a straight line that connects end members of the mixture. However, such a line can be equally regarded as a Sm–Nd isochron if all data points repre-

sent cogenetic geological substances. In this case, the alignment of data points fits the well-known relationship

$$\frac{^{143}\text{Nd}}{^{144}\text{Nd}} = \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_0 + \frac{^{147}\text{Sm}}{^{144}\text{Nd}}(e^{\lambda t} - 1), \quad (2)$$

which is an equation of the straight line, the slope of which is proportional to the age and the intercept corresponds to the initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio.

Thus, according to the requirement of material balance, data points of the untreated SF, leachate, and residue should lie along a straight line in the $^{147}\text{Sm}/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ plot. This line may be either an isochron or a line of mixing. If an authigenic clay mineral was crystallized under conditions of isotopic equilibrium with the fluid, the Sm–Nd isotopic system of which fits that of the leachate, the straight line is an isochron that determines the age of isotopic equilibration. Similarly, the calculated date may approach the average age of rocks from the provenance for the detrital clay and accessory minerals derived from a common provenance. However, if the mobile Nd contained in leachate was never equilibrated with authigenic clay minerals or if the size fraction contains both authigenic clayey material and soluble detrital mineral with inherited Nd, the straight line will reflect the mixing of noncogenetic end members, and the date calculated from its slope will be devoid of geochronological sense.

It is evident that the comprehensive study of leachates and residues for varisized SFs enables us to establish not only the existence (or absence) of isotopic equilibrium between soluble mineral phases and clayey material, but also the presence of the mixed systems within both soluble and silicate materials. If the leachates and/or residues include a mixture of more than two components, the $^{147}\text{Sm}/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ plot will display an appreciable scatter of data points. Interpretation of the two-component mixtures of clay (and/or soluble) minerals is more difficult. As follows from Eqs. (1) and (2), data points of silicate residues (and/or leachates) in the plot lie along the straight line. Nevertheless, the Rb–Sr systematics of clayey rocks show that the mineralogical (for solid components) and chemical (for both solid and dissolved components) study of leaching products can help us to discriminate the lines of mixing from isochrons (Clauer et al., 1997; Gorokhov et al., 2001b, 2002, 2006). In particular, if the data points of leachates (or residues) in the $^{147}\text{Sm}/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ plot lie along a straight line that corresponds to unrealistic age, such a line should be regarded as a mixing line and the respective components should be regarded as isotopically heterogeneous ones. The graphic presentation of data in coordinates $1/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ also may be helpful in this respect.

Trends in the $^{147}\text{Sm}/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ plot (Figs. 5a, 5c) testify to the existence of two-component mixtures in both silicate material and leachates within certain ranges of size SFs, although the relationships of mixing are not perfect here. With allowance for the Rb–Sr data, according to which SF < 0.1 μm of blue clays contains the youngest generation of illite only partly mixed with the rest of clayey material (Gorokhov et al., 1994), the slope of the approximating straight line for residues of SF 0.1–2.0 μm is negative and certainly

devoid of geochronological sense (Fig. 5c). At the same time, the slope of the straight line for leachates corresponds to the age of 770 ± 110 Ma (Fig. 5a), which is much older than the stratigraphic age of the Lontova clay. Since the interpretation of the isochron line for leachates would imply isotopic equilibrium between accessory phosphates and carbonates 770 Ma ago, i.e., before deposition of the Lontova clay, both minerals should be terrigenous ones delivered from a provenance. Apatite is commonly well preserved in sediments. Primary (unaltered) apatite grains are observed under a microscope in thin sections or detected with the SEM (Barnes et al., 1973; Epstein et al., 1977; Lindstrom and Ziegler, 1981). Preservation of carbonate mineral, which is chemically unstable under supergene conditions, seems unrealistic. Furthermore, results of the mineralogical and Rb–Sr study of the Lontova clay (Gorokhov, 1994; Kirsimäe et al., 1999a, 1999b) do not cast any doubt in the authigenic origin of the low-temperature illite concentrated in the finest SF together with the accessory carbonate. Thus, we deal with the mixing of noncogenetic components in both the dissolved material of leachates and the residues, and the slope of the respective trend in Fig. 5a apparently has no geochronological sense. The mixed character of Sm–Nd systems in leachates and residues is also illustrated by relationships in the $1/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ plot (Figs. 5b, 5d).

At the same time, assumption of the pairwise cogenetic relationship between clay and accessory minerals in the Lontova clay seems to be quite sensible. Indeed, the detrital 2M_1 illite in SF 0.6–2 μm could be formed simultaneously and in isotopic equilibrium with apatite microinclusions, which are also concentrated in the coarsest SF, whereas the authigenic 1M – 1M_d illite in SF < 0.1 μm could be formed simultaneously with the REE-bearing carbonate (ankerite?) microinclusions. Previous investigations have shown that such relations are observed, at least, in the Rb–Sr systematics (Gorokhov et al., 1994). If we accept the assumption mentioned above, then analyses of the untreated SF, leachate, and residue for each SF can yield a leachochron (“inner isochron”). Thus, we can determine the apparent age and initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (Fig. 6). The apparent Sm–Nd age of the SFs decreases from 790 to 550 Ma with decrease in the particle size from 0.6–2.0 to < 0.1 μm (Fig. 7a), whereas the initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio increases from 0.51139 to 0.51156 (Fig. 7b), which corresponds to the $\epsilon_{\text{Nd}}(t)$ range from –4.5 to –7.2. The initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are much lower than the values (0.51210–0.51230) known for seawater of the respective time interval (Faure, 1986).

The age variation trend (Fig. 7a) resembles the pattern obtained for the fine-grained SFs of the Lontova clay by the Rb–Sr method (Gorokhov et al., 1994; Kirsimäe et al., 1999a). We can probably state that two generations of mineral with different Sm/Nd ratios and ages (790 ± 90 and 550 ± 100 Ma) are contained in the

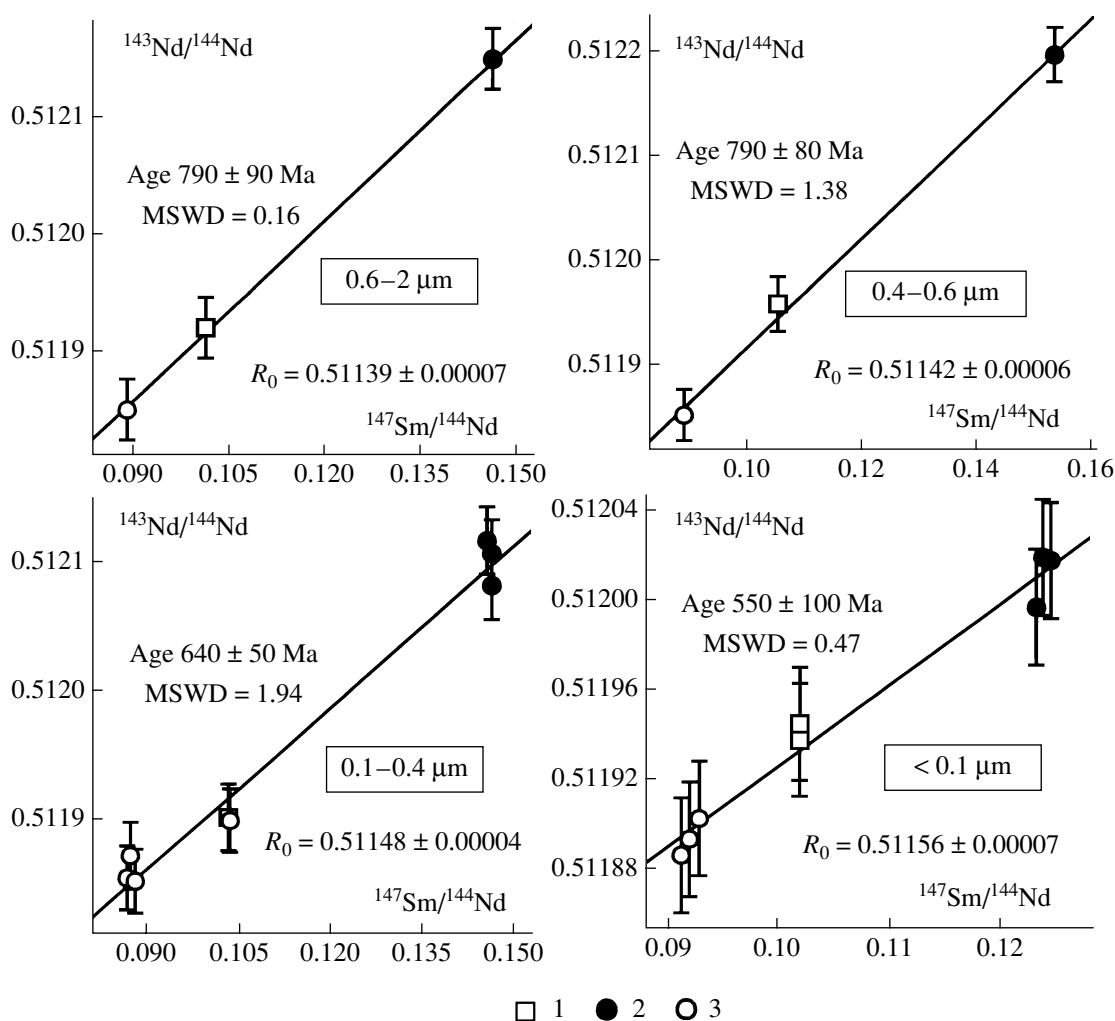


Fig. 6. Internal Sm–Nd isochrons for varisized subfractions. (1) Untreated SF, (2) leachate, (3) residue.

Lontova clay (undoubtedly, in the dissolved form; probably, in the silicate component). The younger date coincides within uncertainty limits with the value of 533 ± 8 Ma obtained with the Rb–Sr method for the fine-grained SFs of the Lontova clay on the basis of the same axiomatics (Gorokhov et al., 1994). This value may be regarded as an additional evidence for the diagenetic authigenic mineral formation in this clay. The great uncertainty of Sm–Nd date for SF < 0.1 μm and the probable occurrence of some amount of older apatite (790 ± 90 Ma) in the mobile component of this subfraction cannot rule out the probability of the formation of a REE-bearing carbonate at the final stage of transformation of the Lontova clay 456–482 Ma ago (Gorokhov et al., 1994; Kirsimäe et al., 1999a; Clauer et al., 2003).

The value of 790 ± 90 Ma for SF 0.6–2.0 μm (Fig. 6) is close to the Rb–Sr age of the coarse-grained SFs of blue clays: 722 ± 13 Ma (Gorokhov et al., 1994) and 860 Ma (Kirsimäe et al., 1999a). This value may be interpreted as the minimal age of provenance of the

Lontova sedimentary material. This interpretation was suggested for Upper Vendian sediments of the Moscow Syncline (Gorokhov et al., 2005; Gorokhov and Felitsyn, 2006). The main part of clay material, including the mixed-layer minerals, was probably delivered to the Lontova sedimentary basin from the northeastern and southwestern regions of the East European Platform (Pirrus, 1980), although the southeastern region of Scandinavia cannot also be excluded as a probable provenance (Puura et al., 1987; Kirsimäe et al., 1999a).

The detrital clayey material of the Late Riphean apparent age is inherent to Vendian–Cambrian sediments in many regions of the East European Platform (Gorokhov et al., 2005). The Rb–Sr and K–Ar dates of whole-rock samples and clay fractions (500–760 Ma) have been obtained for Upper Vendian mudstones of the Nagoryany Formation in the Podol area of the Dniester region (Boiko et al., 1984; Mel'nikov et al., 1990) and the Gavrilov Yam Formation in the Moscow Syncline (Vinogradov et al., 2002, 2003, 2005; Gorokhov et al., 2005). Therefore, we assume that the sedimen-

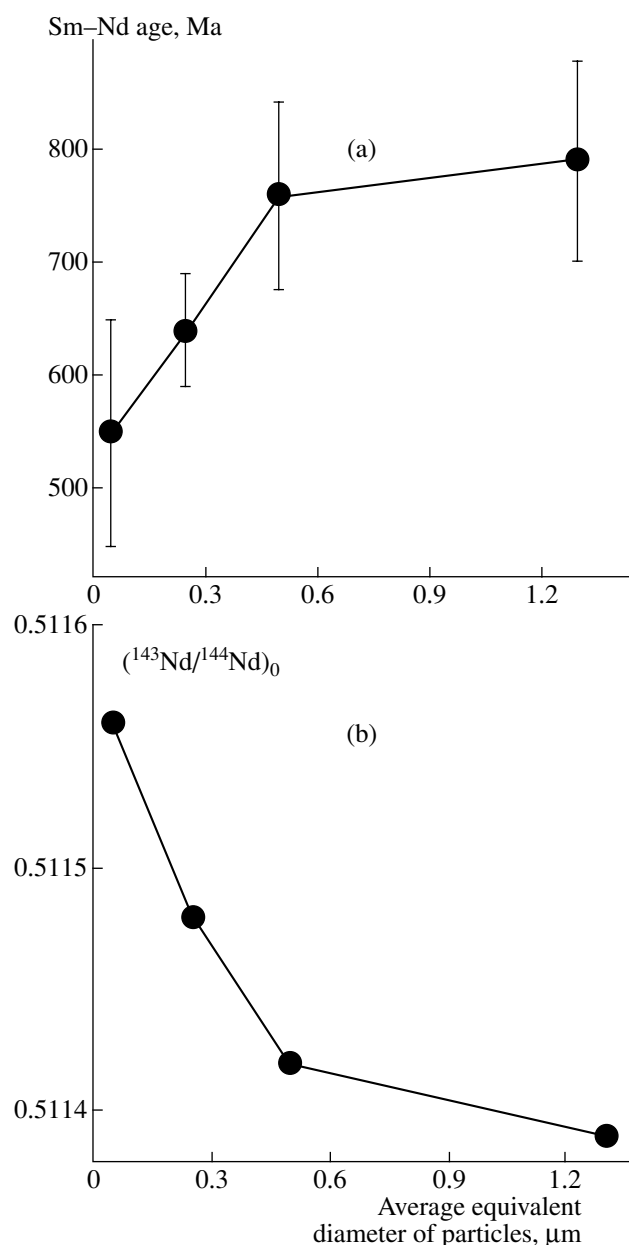


Fig. 7. Parameters of internal Sm–Nd isochrons vs. size of clay particles in subfractions: (a) Sm–Nd age, (b) apparent initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio.

tary cover was rather homogeneous over a significant area of the East European Platform in the Upper Vendian–Lower Cambrian and was derived from provenances with a similar age.

Additional information concerning the geochemical history of the Lontova blue clay may be obtained from the model $t_{\text{Nd}}(\text{DM})$ ages that estimate the residence time of Nd contained in clays of the Earth's crust. The $t_{\text{Nd}}(\text{DM})$ values for both untreated SFs and silicate residues fall into a narrow range of 1.6–1.7 Ga. Assuming that Sm and Nd isotopes did not fractionate during weathering, transport, and sedimentation (McCulloch

and Wasserburg, 1978; Taylor and McLennan, 1985; Chaudhuri et al., 1992), the pre-Riphean crystalline basement of the East European Platform may be regarded as a primordial source of clastic material for the Lontova sediments. Constancy of the $t_{\text{Nd}}(\text{DM})$ values for varisized SFs has the following methodological significance: this fact also rules out any appreciable differential mobility of Sm and Nd in the postsedimentary transformation of the Lontova sediments, although multifold processes of the dia- and catagenetic recrystallization of illite accompanied by the formation of new generations of illite have been recorded here (Gorokhov et al., 1994; Kirsimäe et al., 1999a, 1999b).

CONCLUSIONS

The fulfilled work allows us to draw conclusions concerning both the methodology of the isotopic study of clayey rocks and the practical geochronology.

(1) First of all, it is evident that REE concentrations in the silicate and soluble components of blue clays are favorable for their study with the Sm–Nd method. It has been established that, in terms of the Sm–Nd systematics, both clayey and soluble constituents of the fine-grained subfractions represent mixtures of noncogenetic (probably, different-age) components. Hence, estimation of the suitability of varisized fine-grained SFs for the Sm–Nd dating of stages of the geological history of clayey rocks must be based on the detailed study of isotopic systematics of mixing.

(2) Taking the previously obtained Rb–Sr and K–Ar ages into account, we can assume that the authigenic mineral formation in the Lontova blue clay continued until the Ordovician. However, late stages of the clay material evolution recorded in the Rb–Sr and K–Ar systematics are not detected by the Sm–Nd method. The minimal age of source for the Lower Cambrian sediments in northern Estonia is 750–850 Ma. Therefore, Riphean rocks of the East European Platform seem to be the most probable provenance, although data on the Sm–Nd systematics suggest that the pre-Riphean crystalline basement of this platform likely was a primary source of clastic material in the Lontova sediments.

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