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GEOCHEMICAL CHARACTERIZATION OF SOME ESTONIAN METABENTONITES

Enli KIIPLI and Toivo KALLASTE

Geoloogia Instituut (Institute of Geology), Estonia pst. 7, EE-0001 Tallinn, Eesti (Estonia)

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Abstract. The X-ray fluorescence analysis of chemical elements, supported by X-ray diffractometric mineralogy, shows a change in the composition of main and trace elements in the Palaeozoic altered tephra layers, metabentonites, compared to the unaltered potential source volcanics. As the correlation analysis gives several associations of elements, including that of immobile elements, a source volcanic composition based on Nb/Y and Zr/TiO_2 ratios can be found for 36 Estonian metabentonite samples. Most of these metabentonites are of rhyodacite/dacite and trachyandesite origin, the smaller part derives from rhyolitic and trachytic source magma.

Key words: Estonia, metabentonite, chemical composition, Lower Palaeozoic.

INTRODUCTION

In Estonia Palaeozoic volcanic tephra layers, metabentonites (MBs), have been investigated by Jürgenson (Юргенсон, 1958, 1964, 1988), Utsal and Jürgenson (Утсал & Юргенсон, 1971), Vingisaar (Вингисаар, 1972), and Vingisaar and Murnikova (Вингисаар & Мурникова, 1973) since 1950s. The main characteristic features of Palaeozoic MBs or K-bentonites, as they are called in other countries, are their illite-smectite mixedlayer composition, the presence and secondary origin of potassium, due to its absorption from seawater (Юргенсон, 1958) or to hydrothermal processes during illitization (Brusewitz, 1986; Hay et al., 1988), and the absence of original unaltered vitric material. However, there are numerous exceptions concerning mainly the mineralogical composition: the layers consisting of kaolinite (Лапинскас, 1965; Snäll, 1978) or K-feldspar (Hay et al., 1988) or their mixtures with illite-smectite are found. The aim of geochemical investigations is to detect the original magma composition, locality, and tectonic setting of the source volcanoes and to find out correlations between layers over great distances (Huff & Kolata, 1989; Bergström et al., 1992; Huff et al., 1993). The correlation of the Middle Ordovician MBs, especially concerning "Big Bentonite" ("BB") or Kinnekulle K-bentonite, is based upon stratigraphically well determined palaeontological data as well as on chemical fingerprinting (Bergström et al., 1995).

This paper attempts to present the chemical composition of MBs, the possibilities of the use of trace elements in determining the original magma composition, and point out the changes that MBs have gone through during diagenesis.

XRF analysis data (elements, ppm; oxides, %)

No.	Sample	Stage	Nb	Zr	Y	Sr	Rb	Th	Zn	Ni	Mn	U	Fe ₂ O ₃	TiO ₂	CaO	K ₂ O	Al ₂ O ₃	MgO	Nb/Y	Zr/TiO ₂	XRD mineralogy	Source magma composition according to Winchester & Floyd (1977)
1	ki38 16	Н	6	198	6	77	56	18	30	10	90	<10	1.48	0.251	0.4	15.3	19.8	0.6	1.07	0.08	K-fsp	Rhyodacite—trachyandesite—trachyte
2	D9	D ₁ /D ₁₁	15	191	14	18	66	20	50	20	100	<10	4.22	0.323	0.4	13.9	19.0	1.0	1.06	0.06	1	Trachyandesite
3	ki17 2	H	8	234	18	274	63	10	10	40	50	<10	1.91	0.635	1.1	13.6	17.6	0.9	0.45	0.04	K-fsp	Rhyodacite/dacite
4	io	Du	12	462	34	17	68	10	10	20	40	<10	2.19	0.422	0.8	13.5	19.9	1.4	0.34	0.11		Rhyodacite/dacite-rhyolite
5	vi151.8	Н	12	287	22	301	75	30	20	60	110	10	1.61	0.785	1.8	13.3	20.2	1.0	0.57	0.04		Rhyodacite/dacite-trachyandesite
6	ki15.5	Н	28	478	37	43	69	10	30	20	50	10	1.65	0.463	1.6	12.9	20.1	2.4	0.74	0.10	K-fsp & i/s	Rhyolite
7	ki17.85	H	28	338	16	40	80	35	0	20	40	<10	1.57	0.298	0.4	12.6	21.8	2.0	1.73	0.11	K-fsp & i/s	Trachyte
8	vi145 7	Н	15	356	24	162	64	16	30	80	60	10	1.57	0.671	2.4	12.2	19.7	1.3	0.62	0.05		Rhyodacite/dacite
9	vi185 1	Н	8	224	6	103	86	31	20	20	140	<10	2.48	0.401	0.5	12.1	20.9	2.5	1.33	0.06		Rhyodacite-trachyandesite-trachyte
10	vi152.1	Н	15	337	27	375	65	34	40	60	40	30	2.07	1.177	1.5	11.9	19.8	1.6	0.57	0.03		Rhyodacite/dacite-trachyandesite
11	vi148.8	Н	12	276	44	361	88	29	30	150	150	30	3.11	1.089	2.6	11.6	19.2	1.9	0.27	0.03		Andesite-rhyodacite/dacite
12	ki15.8	H	29	687	44	71	78	27	30	10	30	<10	1.98	0.657	0.7	10.7	22.1	3.0	0.65	0.10	K-fsp & i/s	Rhyolite
13	vi149 4	Н	32	350	4	66	90	42	10	20	40	<10	1.94	0.331	0.5	10.4	22.6	2.6	8.89	0.11		Trachyte
14	oh191.8	Ja	15	300	32	149	73	15	10	20	70	<10	1.80	0.878	2.2	9.8	21.4	2.7	0.46	0.03	K-fsp & i/s	Rhyodacite/dacite
15	oh411.8	G1-2	25	542	60	- 79	116	17	20	40	40	10	3.30	0.847	0.7	8.9	20.1	3.7	0.42	0.06	K-fsp & i/s	Rhyodacite/dacite
16	oh154.25	K ₁	29	301	14	78	95	28	30	10	80	10	1.51	0.391	0.7	8.6	22.0	4.5	2.15	0.08	K-fsp & i/s	Trachyte
17	vi121.03	H	19	452	17	177	68	31	0	100	20	30	1.86	0.570	0.6	8.6	22.6	2.5	1.09	0.08		Trachyandesite
18	mu105.88	H	12	340	42	81	139	24	40	40	150	<10	4.66	0.475	0.8	8.5	20.9	2.6	0.28	0.07		Rhyodacite/dacite
19	oh465.93	Du	7	239	17	53	111	29	50	30	80	10	2.86	0.522	0.6	8.3	20.5	4.7	0.40	0.05	K-fsp & i/s	Rhyodacite/dacite
20	kp95.15	H	28	295	14	99	91	45	40	30	50	20	3.40	0.525	0.8	8.3	20.8	3.0	2.03	0.06		Trachyandesite-trachyte
21	oh201.46	Ja	17	342	30	108	94	11	40	20	150	30	4.22	0.782	2.9	8.2	20.4	3.6	0.55	0.04	K-fsp & i/s	Rhyodacite/dacite
22	oh154.4	K ₁	25	267	12	67	81	29	10	10	70	<10	1.29	0.380	0.6	8.1	19.2	3.8	2.03	0.07	K-fsp & i/s	Trachyandesite—trachyte
23	vi156.8	H	17	353	56	174	61	26	10	40	40	10	2.76	0.853	1.4	7.9	23.0	2.3	0.30	0.04		Rhyodacite/dacite
24	oh375.06	Gra	17	322	31	111	101	20	30	40	110	10	4.86	1.239	2.9	7.8	17.8	2.4	0.55	0.03	K-fsp & i/s	Andesite-rhyodacite/dacite
25	vi148.0	H	38	785	39	118	95	47	60	40	120	40	3.74	0.934	2.1	7.7	20.7	3.1	0.98	0.08		Trachyandesite
26	oh466.3	D_I/D_{II}	11	214	19	63	119	21	20	20	50	10	3.25	0.429	0.9	7.5	19.3	4.2	0.57	0.05		Rhyodacite/dacite-trachyandesite
27	vi147.5	H	36	850	36	128	80	35	20	120	50	<10	3.41	0.910	0.9	7.3	22.2	3.0	1.00	0.09		Trachyandesite
28	vi173.1	Н	34	477	13	105	99	38	20	30	40	<10	5.47	0.629	0.6	7.3	21.2	3.0	2.66	0.08		Trachyte
29	oh233.4	Ja	40	845	66	90	83	91	20	30	100	50	2.63	1.526	1.1	7.1	26.2	2.6	0.61	0.06	i/s & K-fsp	Rhyodacite/dacite
30	oh307.6	J_2	22	210	13	72	86	30	10	10	60	10	1.45	0.353	0.8	6.6	18.5	4.1	1.65	0.06	i/s	Trachyandesite—trachyte
31	ka4151	D_I/D_{II}	13	183	19	76	132	15	30	20	70	<10	3.69	0.292	0.8	6.3	17.2	3.5	0.66	0.06		Rhyodacite/dacite-trachyandesite
32	oh298.5	.10	19	245	22	102	102	38	110	40	160	10	4.25	0.587	3.8	5.6	18.5	3.4	0.86	0.04	terrigenous?	Trachyandesite
33	vi115.02	H	30	694	28	165	54	37	0	40	50	<10	1.85	0.970	1.2	5.3	25.7	2.5	1.05	0.07		Trachyandesite
34	oh369.12	Н	48	639	60	94	52	47	50	10	30	40	1.72	0.716	0.5	4.2	31.5	1.9	0.80	0.09	kaolinite	Rhyolite-trachyandesite
35	ru488.5	Н	22	400	27	67	65	65	10	20	40	<10	4.14	0.487	0.6	4.0	25.4	2.4	0.81	0.08		Rhyolite-trachyandesite
36	oh369.9	Н	48	614	64	87	41	46	0	20	30	30	1.31	0.664	0.5	3.6	25.6	1.4	0.74	0.09	kaolinite	Rhyolite
00		STD	1	2	2	2	3	2	19	5	36	6	0.38	0.014	0.027	0.057	0.8	0.1				

vi, Viki core; oh, Ohesaare core; ki, Kirikuküla core; ka, Kaugatuma core; kp, Karja—Pärsamaa core; mu, Mustjala core; ru, Ruhnu core; pa, Pääsküla quarry; jo, Jõhvi quarry; K-fsp, sample with potassium feldspar prevailing; K-fsp & i/s, sample containing potassium feldspar and illite—smectite; STD, standard deviation.

ANALYTICAL METHODS

Thirty-six whole-rock samples of Estonian MBs were analysed on trace elements Nb, Zr, Y, Sr, Rb, Th, Mn, Ti, Zn, Ni, and main components K_2O , CaO, Fe₂O₃, Al₂O₃, MgO (Table). As, Cl, S, and Pb were determined, but not included in the Table because their concentrations were under detection limit.

The criterion for the selection of elements was their sufficient content for X-ray fluorescence (XRF) analyses carried out using the apparatus available at the Petrological Laboratory of the Institute of Geology of the Estonian Academy of Sciences (VRA-30, Ag-anode, 30 mA and 50 kV). The approximate impulses in seconds per one percent content of an element are: Nb, Zr, Y — 110 000, Sr — 90 000, Rb — 80 000, Zn — 29 000, Th — 19 000, Pb — 15 000, Ni — 6000, Mn — 5200, Ti, Fe — 1200, Ca — 750, K — 500. The element U was measured, but because of its low content (U has 2500 impulse/sec per 1%, but its content is less than 10 ppm) the values obtained are of qualitative and not quantitative importance. The analytical variation was calculated based on the concentration of MB elements after six measurements of the reference sample and two standard deviations were taken to achieve the 90% confidence limits.

The mineralogical composition of the MB samples was investigated qualitatively by the X-ray diffraction method on the HZG-4 diffractometer using Fe-filtered Co radiation. The rock powder was mixed with several drops of ethyl alcohol and spread on a glass slide. Counting data were collected in the range of 20—44 degrees (2-theta).

SAMPLES

Of the total number of samples analysed, thirty-two belong to the Silurian: Ludlow (Rootsiküla Stage), Upper Wenlock (Jaagarahu Stage), and Llandovery (Adavere, Raikküla, and Juuru stages); four samples come from the Ordovician Caradoc: three from the boundary of the Keila and Jõhvi stages and one from the Keila Stage. Figure 1 shows the sampling localities and gives the sections of three cores and positions of investigated samples. Thirteen MB samples were taken from the Ohesaare drillcore, 12 from the Viki core, 5 from the Kirikuküla core; Jõhvi quarry, Pääsküla quarry, Kaugatuma, Ruhnu, Mustjala, and Karja—Pärsamaa drillcores are each represented by one sample. The investigated samples characterize only a small part of MB layers; for example in the Ohesaare core there are recorded 20 layers in the Jaagarahu Stage, 5 layers in the Jaani Stage, and 20 layers in the Adavere Stage (E. Jürgenson, pers. comm.).

The Silurian deposits of the Ohesaare core represent fairly deep-water clay and marl facies, those of the Kirikuküla core belong to relatively shallow-water marl and nodular limestone facies, whereas the sediments of the Viki core lie between them (Кальо, 1970). The MBs from the Ordovician deposits belong facially to open shelf deposits of medium water depth (Мянниль, 1966).

XRD MINERALOGY

Five MB samples were investigated from the Kirikuküla core and 12 samples from the Ohesaare core. These consist of three main minerals illite (mixed-layer illite—smectite), K-feldspar, and kaolinite — the ratio

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Fig. 1. Location of boreholes and quarries (filled circles) from which MB samples were investigated; positions of MB layers in the Ohesaare, Viki, and Kirikuküla sections. MB samples investigated in the present paper are supplied with names. Stratigraphy compiled by Tarmo Kiipli according to Jeppsson & Männik, 1993; Jeppsson et al., 1994; Nestor, 1994; Perens, 1995; Kaljo et al., 1996, plus unpublished data of δ¹³C.

of which is greatly varying in different samples up to the occurrence of nearly monomineral samples (Fig. 2). Illite was identified by 020 reflection. This method does not permit us to differentiate between illite and mixed-layer illite—smectite. Determination of the K-feldspar type in several Estonian MB samples has revealed the existence of low sanidine.

Among the investigated MB samples, the most frequent are illite (illite—smectite) and K-feldspar-containing samples without kaolinite. According to the X-ray diffractogram, one of the Kirikuküla core samples (ki38.16) consists totally of K-feldspar. Kaolinite was not detected in the Kirikuküla core.

In the Ohesaare core there are two layers consisting mainly of kaolinite (samples oh369.9 and oh369.12). These samples, as well as all samples of the Kirikuküla core with a predominantly K-feldspar composition, come from the Adavere Stage. This may show lateral variation of the mineralogical composition inside one stratigraphical unit depending on different facial conditions of diagenesis, although exact correlation of layers is impossible because of the absence of the criteria for precise identification of coeval layers. One Ohesaare sample (oh298.5) is probably not MB but clay with a low carbonate content according to the X-ray diffractogram.



Fig. 2. X-ray diffractograms of different MB samples. Selected d-values in Å are given on top. a (ki38.16), reflections of only K-feldspar were recorded; b (oh369.93), sample dominated by kaolinite, possibly with a certain amount of illite and some K-feldspar; c (oh307.60), illite (illite—smectite) with K-feldspar admixture, one of the greatest illite feldspar ratios among samples of this type; d (oh298.5), sample possibly dominated by terrigenous material; reflections of quartz (4.255 and 3.343 Å), carbonates (3.033 and 2.89 Å), chlorite (4.73 Å), plagioclase (4.035 Å) are not characteristic of MB samples.

Among other minerals quartz, representing the terrigenous component, is of note. Judging from the intensities of quartz reflections, the terrigenous component is of little importance or is absent in most of the MB samples.

Pyrite, calcite, and dolomite were determined in some samples as random additional minerals. Biotite is very common and visually detected in most of the samples. Zircon is a prevailing heavy mineral (20— 60% from the 10% content of heavy minerals in sand—silt fraction which makes up to 10% of the sample) (Юргенсон, 1988).

CHEMICAL COMPOSITION

The chemical data presented in the Table are arranged according to the K_2O content in MB samples. As the mineralogical investigations have proved, the K_2O content depends proportionally upon the K-feldspar amount. In the samples with the K_2O content over 10%, K-feldspar is supposed to dominate. The samples with the K_2O content of 6—10% are considered to have the composition with illite—smectite prevailing. The samples with the K_2O content less than 6% belong to the group containing kaolinite. Great variation of the K content is probably connected with K incorporation into the source volcanic material or its leaching out during diagenesis.

The content of Al_2O_3 varies from 18 to 32%. The comparison of Al_2O_3 in MB with that of igneous rocks shows higher values for MB. The maximum Al_2O_3 content occurs in kaolinite samples exceeding that of rhyolite by about two and a half times. Theoretically, there is no possibility for aluminium to dissolve and move away in seawater as it is insoluble in pH 4—10 (Войткевич & Закруткин, 1976); so there must occur residual enrichment in MBs. Another difference from igneous rocks is the absence or a very low content (<2%) of Na₂O (Юргенсон, 1964; Вингисаар & Мурникова, 1973) indicating the leaching out of sodium.

Silica in MB in no case reaches its content in rhyolite. This does not refer to the basic composition of the original magma source, but more probably shows silica leaching out.

CORRELATION ANALYSIS

The correlation analysis of the chemical elements in MB yields several stronger (correlation coefficient >0.54) and weaker associations:

(1) Strong Y—Th—Nb—Zr—Al affinity (correlation coefficient 0.62— 0.81), weaker correlation of these elements with U and Ti, and negative correlation with K.

The elements Y, Th, Nb, Zr, and Ti are of note as immobile elements (Rollinson, 1993) not altering during weathering processes. The best correlation is between Nb—Zr and Nb—Th (0.81), that of Zr—Y and Zr—Th is weaker (0.73), Y—Nb and Y—Th have the correlation coefficients 0.67 and 0.63, respectively. Since these elements form a group with good positive correlation, they supposedly behave similarly in enrichment and depletion processes during diagenesis.

The positive aluminium and negative potassium correlation for the whole MB sample set can be explained by the greater content of Y, Th, Nb, and Zr in kaolinitic samples that are poor in potassium and rich in aluminium.

(2) Strong Sr—Ni correlation (correlation coefficient 0.68) and their weaker correlation with Ti. This is probably connected with the basic

component of volcanic ash. Ni contents of 80—150 ppm are recorded in the Adavere Stage in four samples from the Viki core. Greater values of Sr are also detected in the Viki core, where the layers with higher Sr values alternate with those having lower values, and in one sample from the Kirikuküla core. In other cores investigated the analogous layers are either absent or not sampled in the present study.

(3) The Rb-Mg-Fe association probably occurs in biotite.

(4) The Mn—Ca association characterizes calcite and dolomite, where substitution of Mn for Ca takes place.

(5) The weak Fe—Mn association characterizes substitution of Mn for Fe in biotite or in some other additional minerals with the exception of pyrite.

(6) Weak positive correlation of Zn with Mn, Fe, Ca, and Rb seems to have an occasional character.

USE OF IMMOBILE ELEMENT DATA

Immobile elements Nb, Y, Zr, and Ti and their ratios are used for the discrimination between different magma series (Winchester & Floyd, 1977) and tectonic settings (Pearce et al., 1984, cited in Huff et al., 1993).

The analysis of the kaolinitic MB samples revealed nearly three times higher contents of immobile trace elements compared to the mean rhyolite content after Winchester and Floyd (1977): Nb 16 ppm vs 49 ppm, Zr 219 ppm vs 639 ppm, Y 26 ppm vs 64 ppm, TiO_2 2000 ppm vs 7100 ppm. Supposing the origination of these elements from the rhyolitic magma, there occurred residual enrichment with them in kaolinites. This suggestion supports the conclusion derived from aluminium enrichment in the same samples. Evidently, there have been great changes in the composition of the source volcanic material, connected mainly with the Si and K movement. For this reason, the absolute values of immobile element contents should be used with caution; element ratios would be applied instead.

ORIGINAL MAGMA COMPOSITION

The scheme worked out by Winchester & Floyd (1977) for geochemical discrimination of different magma series using Nb/Y and Zr/TiO_2 ratios allows us to determine the original magma composition for MBs discussed in the present paper (Fig. 3). As seen from the diagram, samples of the subalkaline suite range from the rhyodacite/dacite field to the rhyolite field. Several samples fall into the trachyandesite field near the border of rhyolites. The "BB" samples taken at the border of the rhyodacite/dacite field sciencide with the data on K-bentonites from British Caradoc (Huff et al., 1993).

The presence of the alkalic trachyandesite—trachyte range is worthy of note. The sample of the most peralkalic origin (No. 13, vil49.4) (Fig. 1) comes from the Adavere Stage (Upper Llandovery). A problem arises with establishing the source area of the alkalic magma as there is very little evidence of Caledonian alkalic volcanism in the surrounding areas. In Norway there are registered some restricted occurrences of alkaline igneous rocks (syenites), for example in Vesteralen and Lofoten islands, in Velfjord and Mosjoen in the Bindal and Vefsen districts, and potassium-rich granites in the Stavanger area (Holtedahl, 1960). Mineralogically, the MBs from the trachyte field containing K-feldspar and illite smectite in different proportions, are all depleted of Nb, Y, Zr, and Ti in comparison with data for unaltered rocks by Winchester and Floyd (1977).



Fig. 3. Samples plotted on the magmatic discrimination diagram of Winchester & Floyd (1977). Centre of a cross marks the location of the average ratio of a sample given in the Table. The size of the cross shows the analytical variation of the ratio (±2 standard deviation in numerator and denominator). Filled quadrangles denote three Caradocian "BB" samples. One sample from the trachyte field (No. 13) has the maximum confidence limit of Nb/Y ratio up to 53 and is not plotted in whole length.

DIAGENESIS

The enrichment—depletion phenomenon indicates the changing of the bulk of initial compounds of volcanic substance. Sporadic chertification of the MB-adjacent rocks (Юргенсон, 1966) is an evidence of silica dissolution from the volcanic ash. Chertification of Silurian fossils resulting from the Silurian tephra is described also by Laufeld and Jeppsson (1976).

Kaolinite was probably formed in the simultaneous process of dissolution and precipitation of original volcanic substance in the acidic environment caused by a high content of organic matter. In Ohesaare clays the content of organic matter, determined as loss on ignition at 500 °C, is c. 4%. In Lithuania Lapinskas (Лапинскас, 1965) described the formation of kaolinitic bentonites in Silurian graptolitic argillites from volcanic ash in the acidic environment. La Iglesia Fernandez and Martin Vivaldi (1972) (cited in Snäll, 1978) found that kaolinite formation was favoured by organic agents.

The depletion mentioned above may to some extent be caused by potassium absorption from seawater. The formation of potassium-containing minerals increases the volume of source substance, whereas the percentage of Nb, Zr, Y, and other immobile elements stay minor in comparison with their original content in whole rock.

The conditions determining the genesis of either illite—smectite or K-feldspar are still problematic. Since the mineralogical types of rock are distributed irregularly between original magma fields in the Winchester—Floyd diagram, a different volcanic source cannot be the only reason for a varied mineralogical composition. One explanation to the variation of the mineral assemblage might be the combination of diverse facial conditions with the different composition of volcanic source that influences the ratio of illite—smectite and K-feldspar.

CONCLUSION

The application of the Winchester—Floyd magma differentiation diagram has revealed MBs of the subalkaline suite ranging from the rhyodacite/dacite field to the rhyolite field, and an alkaline—peralkaline suite ranging from trachyandesite to trachyte source composition. The Ordovician "BB" samples fell within the border area of the rhyodacite/dacite and trachyandesite fields. The alkaline and peralkaline unaltered rocks are characterized by a high Nb content, but in our case the mean Nb values are up to five times less. The values of Y have also decreased. So, the only basis for establishing the alkaline—peralkaline source is the characteristic ratio of Nb and Y. In order to prove the given assumptions, further investigation of alterations in diagenetic processes is needed.

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REFERENCES

- Bergström, S. M., Huff, W. D., Kolata, D. R. and Kaljo, D. 1992. Silurian K-bentonites in Iapetus Region: A preliminary event-stratigraphic and tectonomagmatic assessment. — Geol. Fören. Stockh. Förh., 114, 327—334.
- Bergström, S. M., Huff, W. D., Kolata, D. R. & Bauert, H. 1995. Nomenclature, stratigraphy, chemical fingerprinting and areal distribution of some Middle Ordovician K-bentonites in Baltoscandia. — Geol. Fören. Stockh. Förh., 117, 1—13.
- Brusewitz, A. M. 1986. Chemical and physical properties of Paleozoic potassium bentonites from Kinnekulle, Sweden. — Clays and Clay Minerals, 34, 4, 442—454.
- Hay, R. L., Lee, M., Kolata, D. R., Matthews, J. C., Morton, J. P. 1988. Episodic potassic diagenesis of Ordovician tuffs in the Mississippi Valley area. — Geology, 16, 743—747.
- Holtedahl, O. (ed.). 1960. Geology of Norway. Norges Geologiske Undersokelse. Oslo.
- Huff, W. D., Kolata, D. R. 1989. Correlation of K-bentonite beds by chemical fingerprinting using multivariate statistics. — In: Cross, T. A. (ed.). Quantitative Dynamic Stratigraphy. Prentice Hall, New York, 567-577.
- Huff, W. D., Merriman, R. J., Morgan, D. J., Roberts, B. 1993. Distribution and tectonic setting of Ordovician K-bentonites in the United Kingdom. — Geol. Mag., 130 (1), 93-100.
- Jeppsson, L., Männik, P. 1993. High-resolution correlations between Gotland and Estonia near the base of the Wenlock. — Terra Nova, 5, 348-358.
- Jeppsson, L., Viira, V., Männik, P. 1994. Silurian conodont-based correlations between Gotland (Sweden) and Saaremaa (Estonia). — Geol. Mag., 131 (2), 201—218.
- Kaljo, D., Kiipli, T., Martma, T. 1996. Carbon isotope event markers through the Wenlock. Pridoli sequence in Ohesaare (Estonia) and Priekule (Latvia). — Paleo., Paleo., Paleo. (in press).

La Iglesia Fernandez, A., Martin Vivaldi, J. 1972. A contribution to the synthesis of kaolinite. Proc. Intern. Clay Conf., Madrid, 173—184.

Laufeld, S., Jeppsson, L. 1976. Silicification and bentonites in the Silurian of Gotland. -Geol. Fören. Stockh. Förh., 98, 31-44.

Nestor, V. 1994. Early Silurian Chitinozoans of Estonia and Latvia. Academia, 4. Estonian Academy Publishers, Tallinn.

Perens, H. 1995. Jaani ja jaagarahu lademe piirikihtidest Saaremaal. — Bull. of Geol. Surv. Est., 5/1, 12—19.

Pearce, J. A., Harris, N. B., Tindle, A. G. 1984. Trace element discrimination diagrams for the tectonic interpretation of granite rocks. — J. Petrol., 25, 956—983.

Rollinson, H. 1993. Using Geochemical Data: Evaluation, Presentation, Interpretation. Longman Scientific & Technical. New York.

Snäll, S. 1978. Silurian and Ordovician bentonites of Gotland (Sweden). — Stockholm Contributions in Geology, 31, 1-80.

Winchester, J. A., Floyd, P. A. 1977. Geochemical discrimination of different magma series and their differentiation products using immobile elements. — Chemical Geology, 20, 325—343.

Вингисаар П. 1972. О распространении главного слоя метабентонита (d; XXII) в среднем ордовике Балтоскандии. — Изв. АН ЭССР. Хим. Геол., 21, 1, 62—70.

Вингисаар П., Мурникова Т. 1973. Новые данные о минералогии некоторых нижнекарадокских метабентонитов Эстонии. — Изв. АН ЭССР. Хим. Геол., 22, 2, 149—152.

Войткевич Г. В., Закруткин В. В. 1976. Основы геохимин. Высшая школа, Москва.

Кальо Д. Л. (ed.). 1970. Силур Эстонии. Валгус, Таллинн.

Лапинскас П. П. 1965. Метабентониты нижнего силура Литвы. — Іп: Геология и нефтеносность палеозоя Южной Прибалтики. Гос. геол. ком. СССР, Тр. Ин-та геол., вып. 1. Вильнюс, 49—63.

Мянниль Р. М. 1966. История развития Балтийского бассейна в ордовике. Валгус, Таллинн.

Утсал К., Юргенсон Э. 1971. Минералогия метабентонитов Эстонии. — Изв. АН ЭССР. Хим. Геол., 20, 4, 336—348.

Юргенсон Э. А. 1958. Метабентониты Эстонской ССР. — Тр. Ин-та геол. АН ЭССР, II, 73—85.

Юргенсон Э. А. 1964. Силурийские метабентониты Эстонской ССР. — In: Литология палеозойских отложений Эстонии. Таллинн, 87—100.

Юргенсон Э. А. 1966. Литология лландоверийских отложений Эстонии. Таллинн.

Юргенсон Э. А. 1988. Осадконакопление в силуре Прибалтики. Валгус, Таллинн.

MÕNEDE EESTI METABENTONIITIDE GEOKEEMILINE ISELOOMUSTUS

Enli KIIPLI, Toivo KALLASTE

Siluri ja ordoviitsiumi metabentoniitide keemiline ja mineraloogiline analüüs viitab algse vulkaanilise materjali muutustele. Võrreldes eeldatava algmagma koostisega on vähenenud naatriumi ja räni hulk, alumiinium kui mitteliikuv element on jäänud paigale ning mõnel juhul jääkrikastunud. Kaaliumisisalduse suurenemine on seotud selle lisasissekandega, näiteks mereveest. Mikroelementidest on paigale jäänud immobiilsed elemendid, kuid ka nende sisaldus ei vasta algmaterjali omale. Põhjus on samuti jääkrikastumine või suhteline vähenemine, mis kaasneb aine koguhulga suurenemisega, näiteks kaaliumi sidumisel kaaliumpäevakivisse. Eeldades immobiilsete elementide sisalduste suhete säilimist, on võimalik Winchesteri ja Floydi (1977) magma diskriminantdiagrammi abil leida algmagma koostis Nb/Y ja Zr/TiO₂ järgi. Uuritud 36 proovi puhul ilmneb, et põhiosa pärineb rüodatsiitsest/datsiitsest ja trahhüandesiitsest, väiksem osa rüoliitsest ja trahhüütsest algmagmast.

ГЕОХИМИЧЕСКАЯ ХАРАКТЕРИСТИКА НЕКОТОРЫХ ЭСТОНСКИХ МЕТАБЕНТОНИТОВ

Энли КИИПЛИ, Тойво КАЛЛАСТЕ

Химический рентгенофлюоресцентный анализ элементов в сочетании с рентгенодифракционным минералогическим анализом указывает на изменения в содержании главных и микрокомпонентов в палеозойских метабентонитах по сравнению с первичным вулканическим материалом. Так как корреляционный анализ выявляет несколько ассоциаций элементов, в том числе и иммобильных, то с помощью магматической дискриминационной диаграммы Винчестера и Флойда (Winchester & Floyd, 1977) можно определить состав первичной магмы по соотношениям Nb/Y и Zr/TiO₂. Из 36 изученных метабентонитов Эстонии большая часть имеет риодацитное/дацитное и трахиандезитное происхождение, меньшая часть — риолитное и трахитное.