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SEVEN SEDIMENTARY ROCK REFERENCE SAMPLES FROM ESTONIA

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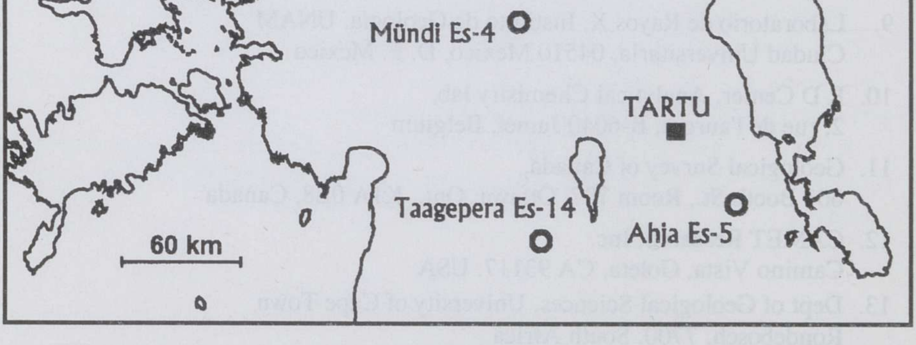
The major oxide and trace element compositions of seven sedimentary rock reference samples (claystone, organic-rich argillite, two limestones, dolostone, sandstone and feldspathized volcanic ash) are presented. Among studied samples the organic-rich argillite ("Dictyonema shale") is conspicuous for wide range of chemical elements with higher contents than in common sedimentary rocks. The content of 68 elements and components has been determined.

Introduction

In the years 1978–80 geological reference samples in the Baltic States and Belarus were prepared. All geological institutions involved compiled their own series of samples, depending on their main research objectives. A total of 409 reference samples was prepared (including 103 Estonian, 129 Latvian, 126 Lithuanian and 51 Belarusian samples) and analysed in the laboratories of all four countries by atomic emission spectroscopy for trace elements and by titration for the main components, using 53 Soviet Union and four German Democratic Republic reference samples. The principles and scope of this work were published in [1].

These reference samples have served for many years as a basis for calibration and control of the analysis quality in the Baltic States and Belarus. To evaluate thousands of analyses made during the last two decades, it was important to calibrate some of these samples at the international level.

Five samples analysed in the present work (Es-1, Es-2, Es-3, Es-4, and Es-5) belong to the series of reference samples of the Institute of Geology of



Location of sampling sites

Tallinn Technical University, Estonia. Two samples (Es-14 and Es-15) were prepared later – in 1996. The sample set includes common silicate and carbonate rocks but also organic-rich argillite (“Dictyonema shale”) characterized by higher content of many elements. The initial weight of the samples was about 5 kg. Rock material selected for sampling exhibits visual homogeneity (except bedded limestone Es-14) and intensive mixing was used to improve it.

In 1998 a project of international calibration of the seven Estonian samples was initiated. An XRF discussion group in the Internet (address: XRF-L@LISTSERV.SYR.EDU) served as a helpful medium for connecting people from laboratories all over the world.

Geological Data of the Samples

The location of sampling sites is presented in the Figure.

Es-1

Silty, mottled, greenish-gray **claystone** of Early Cambrian Lontova age from the central part of the Kestla Member. Sampled from the upper quarry for cement production near the town of Kunda [2].

Es-2

Organic-rich, brown graptolite-**argillite** of Early Ordovician Pakerort age. Sampled in Tallinn from a temporary outcrop at Lasnamäe, 0.5–1.5 m below the upper boundary of the Türisalu Formation [3].

Es-3

Organogenic, gray **limestone** of Middle Ordovician age. Sampled from an old quarry at Lasnamäe (Tallinn), 2.0–2.4 m below the upper boundary of the Väo Formation. Description of the section about 1 km from the sampling site is given in [4, 5].

Es-4

Finely crystalline, gray **dolostone** of Lower Silurian age; Raikküla Stage. Sampled from the Mündi quarry, Central Estonia [6].

Es-5

Mottled gray and red **sandstone** of Middle Devonian age; Burtnieki Stage. Sampled from the Suur-Taevaskoja outcrop near the Ahja River [7].

Es-14

Micritic, yellowish-white **limestone** of Lower Silurian age; Raikküla Stage. Sampled from the Taagepera core (South Estonia) from the depth interval of 319.0–319.6 m. The Taagepera core is stored in Geological Survey of Estonia.

Es-15

Feldspathized volcanic ash of Middle Ordovician age; Kinnekulle bed. Sampled from subsurface tunnels at Pääsküla near Tallinn [8].

Analytical Methods Applied by Different Laboratories

As can be seen in Table 1, this study is mainly based on X-ray fluorescence (XRF) analyses, supported by titration (TI), atomic absorption spectrometry (AAS) and atomic emission spectroscopic analyses (AES) from Estonia, inductively coupled plasma atomic emission spectrometry (ICP-AES) from Finland, Belgium and Canada, and inductively coupled plasma mass spectrometry (ICP-MS) from USA, Canada and Finland. Other methods include determination of H_2O^-, H_2O^+ and loss on ignition, also analyses of Hg (England, Estonia).

Table 1. **Number of Elements Analysed by Different Techniques in Different Laboratories**

Laboratory No. according to the list of the authors' addresses (p. 215)	Techniques						
	TI	AES	AAS	XRF	ICP-AES	ICP-MS	Other
1	12	10		25			2
2				28			1
3				23			
4	3			45			2
5				23	8	25	1
6				27		26	1
7	14	39	5	7			3
8				33			
9				24			1
10					14		1
11	3			21	11	31	1
12				9			
13				29			1

Triplicate or duplicate analyses were applied by most of the laboratories. The average composition (AVG) and standard deviation (SD) were calculated from the main cluster of the analytical results, discarding a few outliers, using the MS97 Excel program. In the cases when standard deviation was bigger than average, the sum of both was considered the detection limit, and the average was marked as below this value.

Comparison of the Present and Former (1978–1980) Values

Comparison of former preferred values with new ones revealed a good agreement as for main components (Tables 2 and 3); old values lying all, except Mg and Ca, within plus/minus one or two standard deviations. A little bit more variable were MgO (within three standard deviations) values and low values of CaO.

Table 2. **Main Components in Silicate Reference Samples, %**

Component	Es-1, claystone			Es-2, organic rich argillite			Es-5, sandstone			Es-15, volcanic ash		
	No.	AVG	SD	No.	AVG	SD	No.	AVG	SD	No.	AVG	SD
SiO_2	11	59.24	0.72	12	52.14	0.99	12	95.10	0.35	8	63.00	0.36
TiO_2	12	0.88	0.05	13	0.76	0.04	13	0.23	0.02	10	0.20	0.02
Al_2O_3	10	17.38	0.35	12	13.15	0.56	12	1.81	0.16	8	18.04	0.10
Fe_2O_3	4	4.29	0.24	1	0.85		5	0.11	0.16	2	0.59	0.06
FeO	4	2.60	0.05	1	3.02		5	1.33	0.08	2	0.14	0.16
MgO	9	2.58	0.07	11	1.11	0.16	8	0.05	0.03	8	0.76	0.04
CaO	12	0.84	0.07	9	0.22	0.02	10	0.047	0.014	9	0.29	0.05
Na_2O	9	0.13	0.04	8	0.10	0.06	7	0.07	0.02	5	0.05	0.04
K_2O	11	5.84	0.17	12	7.95	0.29	11	1.03	0.04	7	14.91	0.23
P_2O_5	12	0.31	0.04	11	0.13	0.04	10	0.022	0.008	7	0.077	0.004
S	7	0.13	0.02	5	2.19	0.16	4	0.01	0.00	2	0.04	0.01
Cl	3	0.05	0.01	2	0.02	0.01	1	0.01		1	0.04	
CO_2	2	0.50	0.04	3	0.07	0.12	3	0.10	0.10	1	0.13	
C_{org}	1	0.03		1	11.10		1	0.00		1	0.07	
H_2O^+	1	4.73					1	0.20		1	1.50	
Total*		99.53			99.57			100.13			99.84	
Total Fe_2O_3	11	7.25	0.22	10	4.35	0.31	13	1.58	0.14	10	0.89	0.07
Total C	2	0.20	0.05	2	11.29	0.30	2	0.06	0.01	1	0.12	
LOI	8	5.21	0.58	7	20.14	0.69	9	–0.03	0.08	5	1.54	0.29
H_2O^-	4	1.68	0.47	4	1.78	0.46	3	0.01	0.02	3	0.56	0.15

*Total for Es-2 includes LOI and does not include S, Cl, CO_2 and C_{org}.

Trace elements (Tables 4 and 5) Ag, Co, Cr, Cu, Ga, La, Nb, Ni, Pb, Sc, Sn, V, Y, Yb and Zn showed also good correspondence (differing by no more than two standard deviations) in Es-1 and Es-2, having typical and a little elevated concentrations for silicate rocks. Low concentrations of trace elements in sandstone (Es-5), limestone (Es-3) and dolostone (Es-4) showed mainly insufficient correspondence exceeding two standard deviations to the values calculated from the present international intercalibration results.

Only Cr, Pb, Ni and Y values correspond well in all samples and both in low and common content levels. Ba, Mn and Sr values were from 1.4 to 5.6 times overestimated in the intercalibration of 1978–1980. It seems that Ba in silicate rocks was overestimated by the factor of 1.4. In the case of Mn, Sr and low Ba, it is not possible to reveal a constant difference factor. Higher than 170 ppm former Zr values well correspond to the new ones, but lower values exhibit insufficient matching.

Table 3. **Main Components in Carbonate Reference Samples, %**

Component	Es-3, limestone			Es-4, dolostone			Es-14, limestone		
	No.	AVG	SD	No.	AVG	SD	No.	AVG	SD
SiO_2	12	4.84	0.96	12	2.84	0.37	8	10.06	0.77
TiO_2	13	0.077	0.013	11	0.041	0.008	9	0.11	0.01
Al_2O_3	12	1.10	0.16	13	0.75	0.17	9	2.12	0.16
Fe_2O_3	2	0.06	0.01	3	0.10	0.17	1	0.28	
FeO	3	0.44	0.14	3	0.35	0.19	1	0.18	
MgO	11	0.85	0.18	9	20.42	0.20	8	1.91	0.05
CaO	11	50.51	0.81	10	29.35	0.50	9	45.68	0.99
Na_2O	9	0.08	0.05	7	0.07	0.08	6	0.08	0.06
K_2O	11	0.51	0.09	12	0.26	0.08	9	0.68	0.14
P_2O_5	9	0.42	0.03	7	0.012	0.003	6	0.023	0.006
S	6	0.12	0.04	7	0.11	0.03	5	0.22	0.08
Cl	2	0.03	0.02	3	0.07	0.03	2	0.03	0.02
CO_2	3	40.67	0.14	5	45.29	0.68	2	37.07	0.47
C_{org}	1	0.00		1	0.00		1	0.33	
H_2O^+	1	0.40		1	0.40		1	0.90	
Total		100.08			100.05			99.67	
Total Fe_2O_3	12	0.61	0.07	12	0.38	0.08	9	0.60	0.07
Total C	2	11.16	0.19	2	12.47	0.18	1	10.52	
LOI	7	40.45	0.20	7	45.33	0.34	6	38.00	0.14
InsRes	2	8.58	1.05	1	4.04		1	12.57	
H_2O^-	3	0.07	0.03	3	0.09	0.03	3	0.17	0.11

Suur-Taevaskoda outcrop, sampling site of Es-5. Foto: E. Kurik

Table 4. **Trace Elements in Silicate Reference Samples, ppm**

Element	Es-1, claystone			Es-2, argillite			Es-5, sandstone			Es-15, volcanic ash		
	No.	AVG	SD	No.	AVG	SD	No.	AVG	SD	No.	AVG	SD
Ag	2	0.12	0.08	3	0.39	0.08	2	<0.1		2	<0.1	
As	2	1.3	0.4	3	37	3	2	<3		3	2.6	0.7
B	1	150		2	53	18	2	23	4	1	40	
Ba	10	420	18	11	379	24	10	147	11	10	119	10
Be	2	3.1	0.1	3	2.4	0.2	3	<1		2	0.9	0.2
Bi	3	<2		3	<1		2	<1		1	0.9	
Cd	3	<1		3	<1		3	<1		2	<1	
Ce	8	111	18	8	63	9	7	27	7	7	19	5
Co	10	20	5	10	12	3	7	2.6	1.0	6	4.0	1.0
Cr	11	78	14	11	80	16	14	31	11	10	9	7
Cs	3	8.8	0.5	2	5.6	0.0	2	0.36	0.04	2	1.18	0.04
Cu	12	25	6	11	105	13	9	10	3	8	6	3
Dy	3	8.3	0.8	3	4.5	0.4	3	1.67	0.12	3	2.8	0.3
Er	3	4.0	0.3	3	2.7	0.2	3	1.09	0.07	3	1.41	0.14
Eu	3	2.5	0.2	3	1.13	0.09	3	0.36	0.04	3	0.29	0.02
Ga	7	23	2	7	16.2	1.3	4	2.1	0.8	7	15	2
Gd	4	10.7	0.5	3	4.78	0.10	3	1.77	0.06	3	2.7	0.2
Hf	4	4.9	0.3	4	3.3	0.4	4	7.3	1.0	4	3.7	0.5
Hg	1	<0.01		1	0.162		1	<0.01		2	0.023	0.000
Ho	3	1.55	0.11	3	0.93	0.08	3	0.36	0.01	3	0.53	0.03
In	1	0.073		1	0.050		1	<0.05		1	<0.05	
La	9	51	7	8	33	6	7	12	2	8	8	3
Li	3	41	8	2	11	8	2	<10		1	100	
Lu	3	0.51	0.06	3	0.41	0.03	3	0.18	0.02	3	0.14	0.03
Mn	11	320	32	11	158	19	11	98	17	6	16	7
Mo	8	<2		9	56	18	7	<2		6	1.0	0.7
Nb	13	16	2	13	14	2	7	3.8	0.7	14	12	3
Nd	5	55	5	5	29	4	5	10	2	5	10	2
Ni	11	40	3	11	98	14	12	9	5	10	6	3
Pb	12	11	2	14	77	17	14	7	4	13	9	4
Pr	3	13.4	1.0	4	7.4	0.4	3	2.7	0.4	3	2.4	0.5
Rb	12	176	8	12	118	5	12	20	2	12	63	3
Sb	1	<1		2	3.0	1.4	1	<1		1	<1	
Sc	8	18	2	9	12	3	7	2.1	0.6	7	4.5	0.7
Se	2	<4		2	2.3	0.4	2	<4		2	<3	
Sm	3	12.2	0.5	3	5.9	0.2	4	1.9	0.3	4	2.5	0.4
Sn	4	3.9	0.2	3	3.2	0.3	1	0.73		3	7.2	1.0
Sr	12	91	6	13	53	7	14	19	4	12	10	3
Ta	3	1.1	0.2	3	1.11	0.09	3	0.29	0.03	4	1.3	0.3
Tb	3	1.59	0.10	3	0.76	0.06	3	0.27	0.01	3	0.48	0.02
Th	10	10.3	2.3	7	11.7	1.3	6	3.4	0.6	9	10.0	1.0
Tl	1	0.72		1	3.13		1	0.12		1	0.55	
Tm	3	0.55	0.04	3	0.40	0.03	3	0.17	0.00	3	0.20	0.01
U	5	2.9	0.6	11	39	5	3	0.81	0.06	8	1.9	0.6
V	10	109	9	10	507	63	8	11	3	8	14	5
Y	13	43	5	13	25	3	10	10	3	12	15	3
Yb	5	3.6	0.4	4	2.8	0.2	4	1.3	0.2	4	1.1	0.1
Zn	11	76	8	11	47	8	8	4	2	9	38	6
Zr	13	176	20	11	133	13	11	302	35	10	112	8

Table 5. **Trace Elements in Carbonate Reference Samples, ppm**

Element	Es-3, limestone			Es-4, dolostone			Es-14, limestone		
	No.	AVG	SD	No.	AVG	SD	No.	AVG	SD
Ag	1	0.07		3	<0.1		2	3.3	1.1
As	1	<1		1	<1		3	4.8	1.8
B	2	21	1	2	12	3	1	20	
Ba	10	29	10	9	14	7	10	211	65
Be	3	<1		3	<1		2	<1	
Bi	1	<0.5		3	<1		3	34	4
Cd	3	<1		2	<1		4	8.1	1.4
Ce	6	13	4	5	6.0	0.7	5	13	3
Co	4	1.8	0.5	5	1.5	1.2	7	5.2	2.1
Cr	11	9	5	12	9	6	11	62	32
Cs	2	0.60	0.00	2	0.25	0.02	2	0.74	0.04
Cu	11	3	2	9	< 4		8	17	6
Dy	3	1.78	0.16	3	0.52	0.05	3	1.20	0.14
Er	3	0.94	0.06	3	0.31	0.02	3	0.65	0.07
Eu	3	0.43	0.03	3	0.14	0.02	3	0.31	0.03
Ga	5	2.2	1.0	5	1.3	0.5	6	3.0	1.3
Gd	3	2.14	0.14	3	0.66	0.14	3	1.46	0.11
Hf	3	0.43	0.03	3	0.42	0.29	3	0.61	0.05
Hg	1	<0.01		1	<0.01		1	<0.01	
Ho	3	0.36	0.03	3	0.10	0.02	3	0.25	0.02
In	1	<0.05		1	<0.05		1	<0.05	
La	7	7.9	1.1	4	2.8	0.5	7	7.5	1.6
Li	2	<10		2	<10		1	<10	
Lu	3	0.09	0.02	3	0.03	0.02	3	0.08	0.01
Mn	12	460	73	11	214	49	10	120	36
Mo	6	<2		6	<2		2	0.8	0.3
Nb	10	1.5	0.7	8	1.0	0.5	11	5.6	1.0
Nd	3	8.6	0.7	4	2.6	0.6	4	7.1	0.4
Ni	9	4	3	9	4	3	7	13	3
Pb	13	5	3	12	4	3	11	127	16
Pr	3	2.04	0.06	3	0.73	0.01	3	1.68	0.06
Rb	11	10	2	11	7	2	12	17	3
Sb	1	<1		1	<1		2	5.8	1.1
Sc	4	1.4	1.2	5	<1.5		6	1.9	0.9
Se	2	<6		2	<3		2	4.4	3.3
Sm	3	1.98	0.17	3	0.58	0.05	3	1.40	0.10
Sn	4	<1		3	<1		3	20	1
Sr	14	178	27	14	32	3	13	492	62
Ta	2	0.09	0.05	2	0.05	0.03	2	0.14	0.02
Tb	3	0.31	0.03	3	0.08	0.02	3	0.21	0.02
Th	7	2.3	1.1	6	0.8	0.4	3	1.5	0.2
Tl	1	0.13		1	0.05		1	0.14	
Tm	3	0.12	0.01	3	0.041	0.002	3	0.10	0.01
U	6	2.6	0.6	3	0.29	0.03	3	0.65	0.06
V	7	9	3	7	11	2	7	12	3
Y	12	13	2	12	4	2	9	7.5	1.0
Yb	4	0.81	0.13	3	0.24	0.03	3	0.56	0.01
Zn	8	4.0	2.1	10	5	3	9	32	7
Zr	9	18	5	7	10	3	6	22.8	1.4

Conclusion

International analytical study of seven Estonian sedimentary rock samples supplied us with the first highly reliable data on the trace elements at low concentration levels characteristic for carbonate rocks and sandstones. Common and elevated contents occurring in Estonian "blue clay" and "Dictyonema shale" are checked in many geoanalytical laboratories of the world including the best ones. Studied samples can serve as reference ones in further analytical works on the geological objects of Estonia.

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