Oil Shale, Vol. 13, No. 4
pp. 341-350

ISSN 0208-198X

THE NATURE OF POTASSIUM IN TREMADOCIAN DICTYONEMA SHALE (ESTONIA)

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Tremadocian Dictyonema shale (argillite) is black argillaceous rock containing 10-20 % organic matter, abundant in sulfur and numerous microelements. Dictyonema shale is characterized by a high potassium and a low sodium content.

Introduction

The high K content of Dictyonema shale has received much attention and the shale ash has been treated as a potential local fertilizer [1, 2]. The reason of such a high K content and its origin are not yet clear.

The results of 68 chemical analyses of drill core samples of Dictyonema shale from western Estonia have yielded K contents ranging from 4.26 to 8.67 % which average 6.57 %. Based on 12 analyses, E. Pukkonen [3] obtained K contents of 2.40-8.0 % that average 6.2 %. In the latter case the shale obviously contained silt interlayers, therefore, the values recorded were lower.

Rocks with a high K content are usually closely related to the weathering area of the palaeobasin. The Dictyonema shale lies on high-maturity Cambrian and Ordovician quartz sandstones. On the erosion surface Cambrian clays were also exposed. The K content of these clays is small: 3.26 % in the Tiskre Formation, 3.70 % in the Lükati Formation and 4.27-4.52 % in the Lontova Formation [4]. In the Baltic Shield, in the northern part of the weathering area, Palaeoproterozoic crystalline rocks cropped out. Among these rocks the K content is highest in rapakivi granites, 4.11-4.88 % [5]. Consequently, the potassium occurring in Dictyonema shale did not originate directly from the weathering area.

Material and Methods of Study

In order to determine the structure of Dictyonema shale and to determine the mineral composition and K distribution in different size fractions, drill hole F238 (geographic coordinates - 59°14.2′ N and 24°36.1′ E) was sampled. This drill hole is located in western Estonia in the region of the greatest thicknesses of the shale. Point samples were taken from the upper (depth 97.2 m), middle (depth 100.2 m) and lower (depth 102.0 m) parts of the Dictyonema shale section. Avoiding quartz silt interlayers only the shale was sampled. The samples were crushed mechanically into pieces of 1-5 mm in size, distilled water was added and the mixture was frozen ten times to -25 °C. The decomposed sample was then dispersed by ultrasound for 15 min. Although the sample was heated in 30 % H_2O_2, not all of organic matter was separated from the clay minerals. Amorphous Fe-Al oxides were separated in Na-citrate and amorphous silica was separated by boiling the sample in 1.0 N NaOH solution.

Different fractions of silt and pelite particles were removed by applying wet sifting, washing and suspension separation in a centrifuge.

The chemical composition, microelements, and K_2O and Na_2O contents in the fractions were determined by chemical silicate analysis, X-ray fluorescence and flame photometry, respectively. The Na_2O content and the weight loss on heating (1000 °C) showed that after chemical processing and fractionating about 8-30 % of the organic matter remained in the shale sample and the finest fraction contained up to 25 % Na_2O. Therefore the K_2O and microelement contents were recalculated to the mineral matter (ash) of the shale. From the latter, in turn, the amount of Na_2O was eliminated as input by separating.

For X-ray diffraction analysis of powders, and for the more precise determination of the layer silicates oriented preparations were used.

Results

In order to establish the source of potassium, it is necessary to determine the origin of the sediments. It can be done by consideration of several different features:

Lithological Characters

Lithological characters - mineral composition, structure and texture, and colour of the rock.

The mineral composition of Dictyonema shale is surprisingly uniform. Notable differences, however, are observed in the distribution of minerals according to grain size. The mineralogical analysis of nine fractions (Table 1) shows that K occurs mainly in K-feldspars and illite. The finest fraction contains excess K in large amounts. The content of K-feldspar is greatest in the fractions from 5 to 63 microns. In coarser fractions the amount of K decreases sharply, in finer ones more gradually. Judging from the crystal lattice levels (-204 and 060), K-feldspar might be considered sanidine. Good disorientation of feldspar grains in the powder preparations shows the absence of cleavage surfaces and preferred growth surfaces in crystals.

The samples are mostly composed of 10-Å-layer silicates. In all fractions a dioctahedral ($d060 = 1.5$ Å) mineral was found. The peak (reflection) full width at half maximum (FWHM) and $d001$ value increase gradually in finer fractions.

Table 1. **X-ray Analysis of Dictyonema Shale**

Sample No.	Fraction, µm	Contents of minerals*, mass %							
		Q	San	M	Ill	h-Ill	Chl	Pyr	Ap
3-1	>100	-	-	-	-	-	-	-	-
3-2	63-100	77.0	11.6	0.0	7.6	0.0	1.1	2.5	0.2
3-3	10-63	42.4	43.6	9.2	0.0	0.0	0.8	3.7	0.4
3-4	5-10	32.8	41.8	22.0	0.0	0.0	1.8	1.2	0.5
3-5	2-5	30.9	37.6	28.6	0.0	0.0	2.2	0.0	0.7
3-6	1-2	23.1	28.8	0.0	44.7	0.0	2.4	0.0	1.0
3-7	0.5-1	15.8	23.5	0.0	57.3	0.0	2.5	0.0	0.8
3-8	0.2-0.5	9.3	18.9	0.0	69.0	0.0	2.8	0.0	0.0
3-9	<0.2	4.7	0.0	0.0	0.0	93.2	2.1	0.0	0.0
Weighted mean**		27.1	32.4	14.4	9.3	13.3	1.9	0.9	0.5
1-1	>100	19.4	28.2	0.0	48.0	0.0	2.7	1.1	0.7
1-2	63-100	40.4	35.7	0.0	20.1	0.0	0.0	3.0	0.9
1-3	10-63	31.6	50.2	15.0	0.0	0.0	0.7	2.0	0.5
1-4	5-10	32.6	38.2	26.2	0.0	0.0	2.2	0.3	0.4
1-5	2-5	31.0	34.2	32.1	0.0	0.0	1.9	0.0	0.8
1-6	1-2	17.3	21.7	0.0	57.9	0.0	2.0	0.7	0.5
1-7	0.5-1	13.1	23.3	0.0	59.6	0.0	3.0	0.0	1.0
1-8	0.2-0.5	6.2	11.7	0.0	79.5	0.0	2.6	0.0	0.0
1-9	<0.2	3.5	0.0	0.0	0.0	96.5	0.0	0.0	0.0
Weighted mean		25.3	30.9	17.7	9.0	14.6	1.7	0.4	0.4
4-1	>100	20.6	38.8	0.0	35.7	0.0	2.5	1.4	1.0
4-2	63-100	29.4	39.0	0.0	29.1	0.0	1.0	1.0	0.6
4-3	10-63	28.9	51.2	16.1	0.0	0.0	1.1	2.0	0.6
4-4	5-10	30.5	39.5	28.0	0.0	0.0	1.5	0.0	0.4
4-5	2-5	29.2	35.0	33.2	0.0	0.0	1.7	0.0	0.9
4-6	1-2	18.6	28.2	0.0	51.1	0.0	1.2	0.0	0.9
4-7	0.5-1	12.1	26.1	0.0	60.7	0.0	0.0	1.1	0.0
4-8	0.2-0.5	7.0	21.2	0.0	71.7	0.0	0.0	0.0	0.0
4-9	<0.2	3.0	0.0	0.0	0.0	95.4	1.6	0.0	0.0
Weighted mean		23.7	33.0	18.1	10.0	13.1	1.3	0.3	0.5

Q - quartz, San - sanidine, M - muscovite, Ill - illite, h-Ill - hydrated illite, Chl - chlorite, Pyr - pyrite, Ap - apatite.

* Method was calibrated using the results of chemical analysis.

** In default of fraction >100 µm, the sum of the weighted is 99.78 %.

Thus, the 10-Å minerals may be considered as a grain-size dependent transitional sequence of muscovite-illite-hydrated illite, which has earlier been treated as montmorillonite hydromica [8].

In the present work the following distribution, based on the 001 reflection half-width (FWHM), was used:

Muscovite	> 2 μm	FWHM < 0.2 2 Θ
Illite	2 > 0.5 μm	0.2 < FWHM < 0.6 2 Θ
Hydrated illite	< 0.5 μm	FWHM > 0.6 2 Θ

The peak FWHM and (*d*001) value increase in the fractions > 10 μm and also growth of 10-Å mineral content in the coarsest fractions show the occurrence of cemented aggregates in fractions > 10 μm where the cementing component is represented by hardened clay particles. The real greatest size of monomineralic grains is in the range of 10-63 μm.

The distribution of quartz by grain size is similar to that of orthoclase. Quartz is mostly well crystallized. According to F. Zukov and V. Petersell [9], the shape and degree of weathering of quartz and K-feldspar grains in Dictyonema shale suggest a tuffaceous origin according to E. Puura (pers. comm.). In electron photo micrographs angular quartz is clearly observed among the clay minerals of the shale. Angular quartz of possibly volcanogenic origin has also been recorded in Tremadocian sediments by T. Kurvits [10].

Table 2. **Grain-Size Analyses of Dictyonema Shale from Drill Core F328, %**

Fraction, μm	Sample No.					
	3		1		4	
	a	*b*	*a*	*b*	*a*	*b*
>100	0.22	0.22	0.20	0.20	0.37	0.37
63-100	0.16	0.16	0.06	0.06	0.11	0.11
10-63	10.21	11.59	10.57	11.54	13.79	14.46
5-10	42.54	46.57	52.77	55.77	44.40	52.69
2-5	14.38	14.52	7.20	7.26	10.44	9.55
2-1	11.63	10.17	7.35	5.86	9.76	7.81
1-0.5	4.39	3.81	3.88	3.07	4.43	3.27
0.5-0.2	2.25	2.23	2.87	2.87	2.97	2.66
<0.2	14.22	10.74	15.10	13.37	13.73	9.08

a - Total after treatment.
b - Recalculated after ashing to 1000 °C (without organic matter and sodium).

In the case of K-rich source material, sanidine is dominant among feldspars [11]. Apart from clay minerals, decomposition of volcanic glass formed free silica, which was deposited from the pore solutions during diagenesis to form silica layers in Dictyonema shale [12]. Therefore the occurrence of X-ray amorphous phases cannot be excluded. The diffuse X-ray maximum in the region 4.2-3.3 Å, treated by R. Palvadre et al. [13] as an inorganic amorphous phase, may be partly caused by very fine-grained quartz and feldspar.

The volcanogenic origin of siliciclastic material in Dictyonema shale and its partial transport via air are also evidenced by the uniform structure of the shale and almost complete lack of the coarser components (Table 2). From the weathering area, the material was transported into the sedimentary basin.

The Dictyonema shale is mostly horizontally bedded. It contains individual quartz silt layers ranging from a few millimetres to some centimetres in thickness. The latter depends on the grain size of the material - coarser material forms thicker interlayers. In the dark organic-rich shale, there are light grey layers of coarse pelite particles devoid of organic matter.

Light layers in the shale indicate abundant influx of tuffaceous material as pointed out by J. Judovich [14].

Petrochemical Characters

Of great importance with respect to the origin of the sedimentary material are relations between oxides (modules) of certain elements and the corresponding module diagrams. Particularly informative among them are:

Titanium module TM = TiO_2/Al_2O_3

Aluminium-silica module AM = Al_2O_3/SiO_2

Iron module IM = $(Fe_2O_3 + FeO + MnO)/(TiO_2 + Al_2O_3)$

Potassium-sodium module PM = SM = $(K_2O + Na_2O)/Al_2O_3$

In the module diagram (Fig. 1) the samples of Dictyonema shale do not fall into fields for normal marine sedimentary rocks. (In the diagram normal sea rocks are represented by Cambrian, Ordovician and Palaeozoic clays of the East European Platform [15].) A distinct anomaly, which may be explained by the presence of volcanogenic sediments, is observed in (PM + SM)/IM and (PM + SM)/AM.

Geochemical Characters

The chemical composition of Dictyonema shale (Table 3) is in good accord with its mineral composition. Differences occur only in the finest fraction where no correlation is observed between the high K content and mineral composition (Table 4).

The contents and distribution patterns of Pb, Sr, Nb, Zr and Rb (Table 4; Fig. 2) permit us to determine the origin of K in Dictyonema shale. The washing out of the above elements during chemical processing and fractionating of samples was insignificant. Neither were these elements concentrated by organic matter.

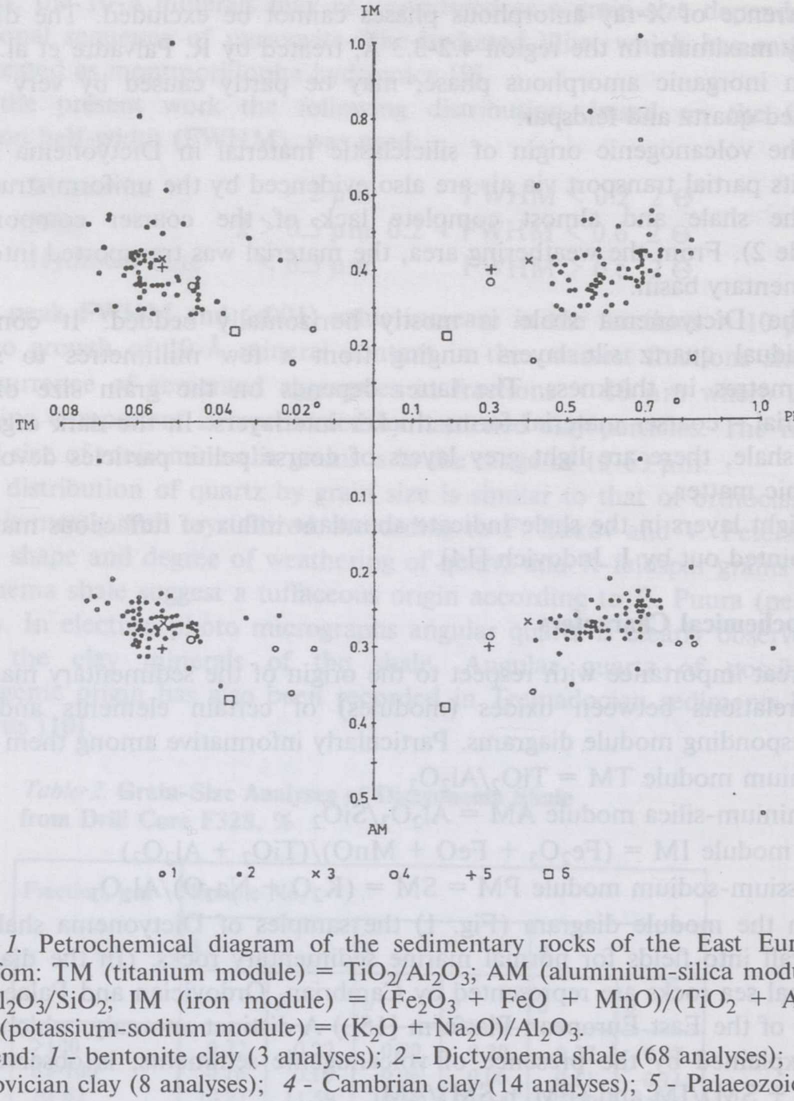

Fig. 1. Petrochemical diagram of the sedimentary rocks of the East European Platfom: TM (titanium module) = TiO_2/Al_2O_3; AM (aluminium-silica module) = = Al_2O_3/SiO_2; IM (iron module) = $(Fe_2O_3 + FeO + MnO)/(TiO_2 + Al_2O_3)$; PM (potassium-sodium module) = $(K_2O + Na_2O)/Al_2O_3$.
Legend: *1* - bentonite clay (3 analyses); *2* - Dictyonema shale (68 analyses); *3* - Ordovician clay (8 analyses); *4* - Cambrian clay (14 analyses); *5* - Palaeozoic clay (401 analyses); *6* - average clay content (after A. Vinogradov)

The Pb content is 2-3 times higher than the clark of clays or granitic rocks, whereas its content increases towards finer fractions reaching a maximum (554 ppm) in the finest one. The contents of Sr, Nb, and Zr are close to the clark of granitic rocks, whereas the Sr content is much lower and the Nb and Zr contents are higher than the clark of clays [16]. The content of these elements increases in the direction of finer fractions, but reaches a maximum in the fraction of 1-2 μm, then starts to decrease afterwards.

Table 3. **Chemical Composition of Dictyonema Shale from Drill Core F328, %**

Components	Sample No.					
	3		1		4	
	Total	A*	Total	A*	Total	A*
SiO_2	49.58	64.73	49.80	65.55	45.20	63.63
Al_2O_3	12.57	16.41	12.57	16.55	12.23	17.22
Fe_2O_3	2.56	3.34	2.05	2.70	1.90	2.67
TiO_2	0.66	0.86	0.66	0.87	0.71	1.00
MnO	0.015	0.02	0.018	0.02	0.017	0.02
CaO	0.35	0.46	0.37	0.49	0.38	0.54
MgO	1.04	1.36	0.86	1.13	0.74	1.04
P_2O_5	0.16	0.21	0.10	0.13	0.12	0.17
FeO	2.44	3.18	2.59	3.41	2.73	3.84
Na_2O	0.06	0.08	0.09	0.12	0.01	0.02
K_2O	7.16	9.35	6.86	9.03	7.00	9.85
LOI	23.91	-	25.13	-	29.20	-
Total	100.51	100.00	101.10	100.00	100.24	100.00
S_{total}	3.15		2.94		3.33	

A* - Recalculated after ashing to 1000 °C of Dictyonema shale.

Table 4. **Potassium (%) and Microelement (ppm) Content of Fine Fraction of Dictyonema Shale***

Sample No.	Fraction, μm	K_2O	Pb	Sr	Rb	Zr	Nb
3-3	10-63	9.47	57	76	140	146	19
3-4	5-10	10.05	56	76	126	191	17
3-5	2-5	9.23	86	124	183	211	33
3-6	2-1	8.54	174	205	246	240	42
3-7	1-0.5	7.95	292	225	316	278	47
3-8	0.5-0.2	7.18	876	168	392	308	40
3-9	< 0.2	12.58	489	92	210	190	9.6
	Weighted mean	9.84	135	116	167	199	23
1-3	10-63	9.55	54	87	142	129	21
1-4	5-10	10.32	55	98	141	138	26
1-5	2-5	8.74	51	118	183	157	25
1-6	2-1	8.47	98	192	253	198	47
1-7	1-0.5	7.63	295	243	353	320	71
1-8	0.5-0.2	7.01	379	180	359	284	43
1-9	< 0.2	7.91	541	123	232	211	30
	Weighted mean	9.51	139	114	175	162	29
4-3	10-63	10.51	56	80	145	137	20
4-4	5-10	10.60	82	107	154	201	35
4-5	2-5	9.90	98	123	197	180	37
4-6	2-1	8.82	204	187	261	237	49
4-7	1-0.5	9.38	350	233	317	320	58
4-8	0.5-0.2	7.63	385	167	375	343	38
4-9	< 0.2	11.81	554	127	321	370	22
	Weighted mean	10.40	152	122	192	216	34

* Recalculated after ashing to 1000 °C of Dictyonema shale.

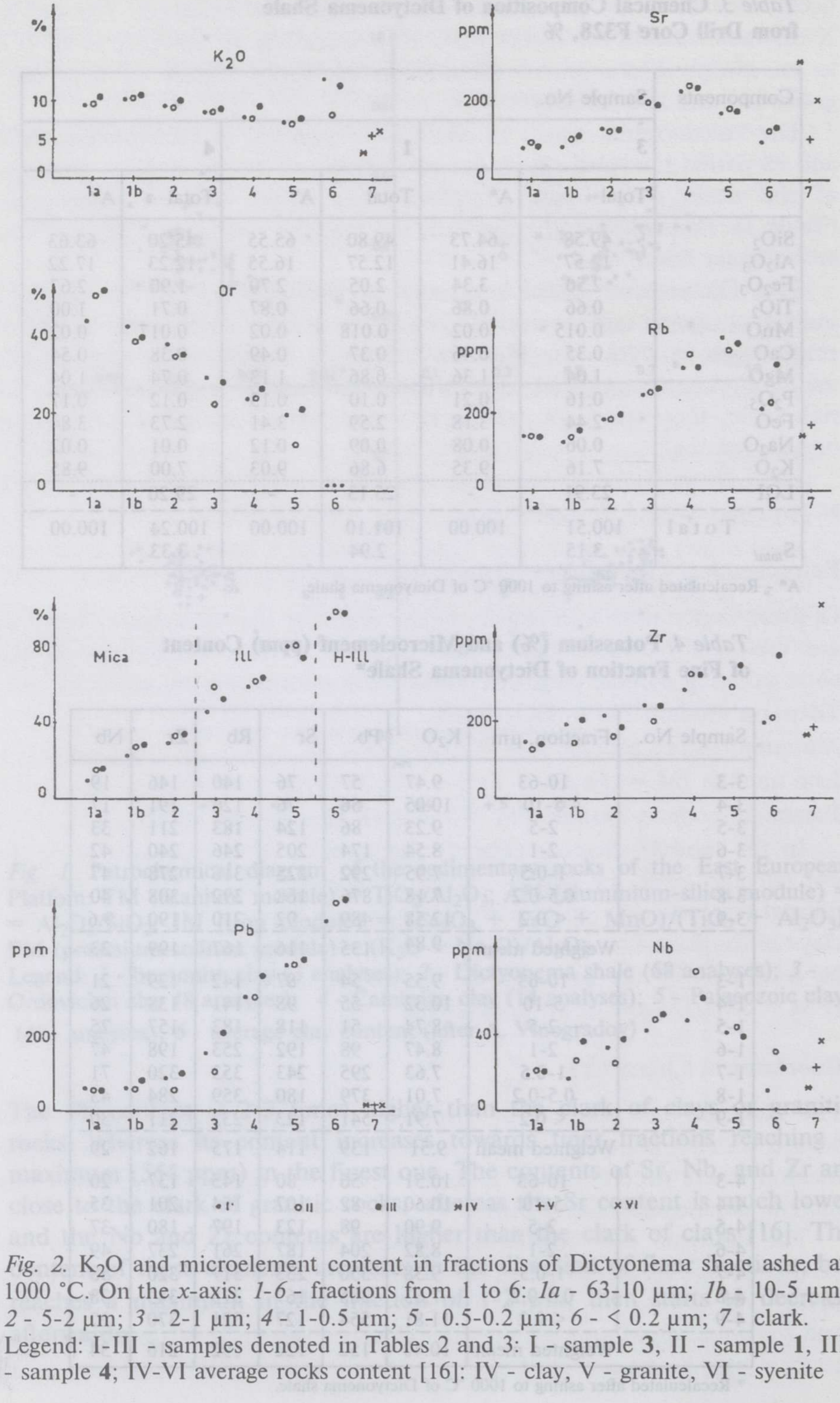

Fig. 2. K_2O and microelement content in fractions of Dictyonema shale ashed at 1000 °C. On the *x*-axis: *1-6* - fractions from 1 to 6: *1a* - 63-10 μm; *1b* - 10-5 μm; *2* - 5-2 μm; *3* - 2-1 μm; *4* - 1-0.5 μm; *5* - 0.5-0.2 μm; *6* - < 0.2 μm; *7* - clark. Legend: I-III samples denoted in Tables 2 and 3: I - sample **3**, II - sample **1**, III - sample **4**; IV-VI average rocks content [16]: IV - clay, V - granite, VI - syenite

The amount of Rb is close to the clarks of clays and granitic rocks, and its distribution is rather similar to that of the above elements.

No distinct correlation was noted between the microelements under discussion, and a high content of K and main shale-forming minerals. Only the Pb content increases with an increase in the content of mica and clay minerals. The relations of other elements are more complex.

The reasons for the distribution of microelements are not completely understood. Undoubtedly, the content and distribution of these elements (first of all Sr and Nb) in the shale suggests a possible occurrence of acid (with features of basic magma) volcanic material, the amount of which increases downwards in the section. The fall of the maxima of Sr, Nb and other elements within the 1-2 μm fraction is probably due to the concentration of the host minerals in this fraction.

Concluding Remarks

The mineral composition and texture of Dictyonema shale are uniform through the whole section. The potassium content is similar in different parts of the section. Potassium occurs in sanidine, micas and illite, which is in good accord with the results of mineralogical and chemical analyses.

Different K contents were found in different grain-size fractions of the Dictyonema shale. The finest fraction contains abundant excess K (< 0.2), which is not related to the minerals analysed but probably to amorphous volcanogenic material. The occurrence of the material of deep origin is also evidenced by several microelements.

Influx of volcanogenic material either directly into the sedimentary basin as airfall toffs or by transport from the weathering area and later diagenetic change in water and sediment was a complex process which needs special study.

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Presented by A. Raukas

Received July 09, 1996