

METHODS FOR THE DETERMINATION OF THE TEXTURE AND MINERAL COMPOSITION OF THE DICTYONEMA SHALE

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The Tremadoc (Lower Ordovician) Dictyonema Shale is an organic-rich lithified clay. To determine its texture and mineral composition, the samples of strongly compacted but not metamorphosed shale were disintegrated, and the organic matter, amorphous Fe- and Al- oxides and amorphous silica were removed.

The shale samples were crushed into 5–10 mm fragments, moistened with distilled water and frozen ten times at -27°C .

30 % hydrogen peroxide was used to oxidate organic matter in samples and the sodium citrate to remove amorphous Fe–Al oxides. Then the samples were boiled in 1 N NaOH solution to remove amorphous silica cement. After every stage the solution was decanted and the samples were washed with distilled water.

To determine the texture of the disintegrated and chemically processed samples, the pelitic and fine silt particles were removed from the suspension by centrifugation (Starkey et al., 1985). The coarse fraction obtained ($>5\mu\text{m}$) was additionally divided into subfractions by repeated washing.

The mineral composition of the Dictyonema Shale was determined by X-ray diffractometry. During preparing the samples and processing diffractograms several special ways were used.

Key words: Dictyonema Shale, organic matter, amorphous oxides, X-ray diffractometry, Ordovician, Estonia.

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INTRODUCTION

The Tremadoc Dictyonema Shale from North Estonia (Petersell, 1997), an organic-rich (10–20 %) brown lithified clay belongs to the formation of black shales which somewhere is related all over the world to sedimentary phosphorites and concentrates numerous metals. The organic matter of the Dictyonema Shale has sapropelic origin and is rich in N, S and O (Table 1). Although the C/H ratio in organic matter is approximately 9, the caloric value of the organic matter of the Dictyonema Shale is modest, on average about 34 MJ/kg.

In the Dictyonema Shale over 12 minor elements are known, the content of which exceeds the average of clays 2–100 and more times (Loog, 1962; Petersell et al., 1981; Pukkonen, 1989).

In Estonia mainly the chemical composition of the shale, including the character of the organic matter and

the areal as well as vertical distribution of chemical elements has been studied (Table 2).

The texture and mineral composition of the Dictyonema Shale have been poorly studied. To determine them, we had to disintegrate the rather compact (though not metamorphosed) rock to remove the organic matter, amorphous Fe and Al oxides and amorphous silica, which bind (cement) clay particles. The task proved not a simple one as it differs greatly from the techniques used for the determination of the texture and mineral composition of clays.

The present paper includes the description of the techniques used for disintegrating the shale. The data about the mineral composition and texture of the Dictyonema Shale, obtained in the course of this study, were exploited for researching the nature of potassium in Dictyonema shale (Loog et al., 1996) and will be used also in further investigations and publications in the future.

Table 1

THE ELEMENT COMPOSITION OF ORGANIC MATTER OF THE DICTYONEMA SHALE

District	Ash (A)%	Organic matter (OM)%	Content of elements in organic matter, %				
			C	H	N	S	O
Maardu	79.2	16.8	70.5	8.3	2.5	2.4	16.3
Toolse	80.5	15.4	69.0	7.6	2.1	2.1	20.2

CHEMICAL COMPOSITION OF THE DICTYONEMA SHALE, %

Compounds	West Estonia		Maardu		Toolse		Average of clay and shale of the world (Vinogradov, 1962)
	Initial shale	Anorganic part	Initial shale	Anorganic part	Initial shale	Anorganic part	
SiO ₂	48.19	64.00	50.87	64.46	48.20	64.56	51.00
TiO ₂	0.68	0.90	0.75	0.95	0.68	0.91	0.75
Al ₂ O ₃	12.46	16.55	12.68	16.07	11.98	16.04	19.74
Fe ₂ O ₃ total	5.04	6.73	4.93	6.25	4.57	6.12	4.77
MgO	0.88	1.17	0.69	0.87	0.77	1.03	2.22
CaO	0.37	0.49	0.31	0.40	0.47	0.63	3.54
Na ₂ O	0.05	0.06	0.04	0.05	0.02	0.03	0.89
K ₂ O	7.01	9.31	7.94	10.06	7.22	9.64	2.75
P ₂ O ₅	0.13	0.17	0.05	0.06	0.19	0.25	0.18
LOI	24.51		20.90		24.89		
Sum	99.32	99.38	99.16	99.17	98.19	99.21	
a.t. FeO	2.60		2.20		2.05		
S _{total}	3.14		2.58		2.45		0.3

DISINTEGRATION OF THE SHALE

To disintegrate the shale, pieces with a weight of 100 g were crushed into 5–100-mm fragments. The crushed sample was moistened with distilled water and frozen at –27°C for two hours, then melted at room temperature. This procedure was repeated ten times. The disintegrated Dictyonema Shale was put into a 0.5-litre boiling tube,

and 250 ml of distilled water and 2.5 ml of peptizator (concentrated liquid ammonia NH₄OH) were added. The boiling tube with the samples was placed into the ultrasonic dispergator and processed for 15 min. In spite of processing the aggregates were recorded in all fractions >0.063 mm (Table 3).

To oxidate organic matter, after mechanical disintegration of shale, 10 ml of 30% hydrogen peroxide (H₂O₂) was poured on it, mixing the sample slowly. Then 5–10 ml of H₂O₂ was added at every 5–10 min. When intensive decomposition (foaming) of organic matter had stopped, the sample was heated to 70°C and some more H₂O₂, all in all up to 100 ml, was added during one hour. Nevertheless, even then organic matter was not completely oxidized.

To remove amorphous Fe–Al oxides, we added 150 ml of distilled water and 14 g of sodium citrate (Na₃C₆H₅O₇ · 2H₂O) and 1.4 g of sodium bicarbonate (NaHCO₃), necessary to keep the pH value at 7.0–7.5 in the solution, were added to the 50-g sample. The suspension was heated to 75–80°C and mixed until the dissolution of amorphous oxides. Next, 3.5 g of sodium hypsulphite was added and the sample was constantly mixed for 5 min. After that the mixing was performed occasionally 10 min. The solution was decanted and the sample washed with distilled water.

To remove amorphous silica compounds, the sample was boiled in the 1 N NaOH solution (the sample/solution ratio 1/2). The solution was decanted and the sample washed with distilled water. The compounds, formed or added at the intermediate phases, dissolved and could have been removed by washing. However, in the finest fraction the NaCl was detected by XRD. That means, that the salts were not removed all at once.

Table 3

THE TEXTURE (GRANULOMETRIC COMPOSITION) OF THE DICTYONEMA SHALE AT A DEPTH OF 98.1 IN BOREHOLE F 338

Particle size, μm	I	Particle size, μm	II
		> 100	0.15
		100-63	0.09
		63-10	12.04
> 5	56.34	10-5	44.06
5-2	12.69	5-2	12.69
2-1	10.07	2-1	10.07
1-0.5	4.31	1-0.5	4.31
0.5-0.2	2.40	0.5-0.2	2.40
< 0.2*	14.19	< 0.2*	14.19
Sum	100 %		100 %

I texture obtained by separation from the suspension using centrifugation;

II texture obtained by additional division of the coarse fraction (5) applying repeated washing;

*total dissolved solid

RESULTS OF THE X-RAY FLUORESCENCE ANALYSIS OF THE DICTYONEMA SHALE, MG/KG

Sample No	Element	Initial sample	Organic matter*	Amorphous Fe-Al oxides**	Amorphous silica compounds***
1	U	132	280	2	< 2
	Th	4.1	22	< 2	< 2
	Pb	84	13	< 2	< 2
	Sr	86	29	< 2	< 2
	Rb	107	41	< 2	< 2
	Mo	146	354	179	266
	Y	41	53	13	4.5
	Zr	131	138	50	40
	Nb	21	3.7	14	8.8
3	U	44	93	< 2	< 2
	Th	4.7	15	< 2	< 2
	Pb	99	7.5	< 2	< 2
	Sr	86	26	< 2	< 2
	Rb	114	32	< 2	< 2
	Mo	85	204	128	199
	Y	38	51	13	2.4
	Zr	136	89	43	32
	Nb	16	< 2	12	7.7
4	U	97	160	2.9	< 2
	Th	3.2	15	< 2	< 2
	Pb	94	13	< 2	2.8
	Sr	87	50	< 2	< 2
	Rb	109	49	< 2	< 2
	Mo	345	785	648	804
	Y	36	21	13	7.5
	Zr	129	112	50	40
	Nb	19	2	15	13

* separated after processing with H₂O₂

** separated after processing with sodium citrate

*** separated after processing with NaOH

DETERMINATION OF THE TEXTURE

To determine the texture of the disintegrated and chemically processed sample, the pelitic and fine silt particles were removed from the suspension by centrifugation (Starkey et al., 1985). The coarse fraction obtained (> 5 µm) was additionally divided into subfractions by repeated washing (Table 3).

The organic matter not separated by preliminary processing binds also pelitic particles in the suspension and they are not removed easily. For separating one fraction, centrifugation should be applied several tens of times. By centrifugation organic matter is often separated also

and forms a dark film on the suspension or on preparations made of it.

Minor elements should be determined from the initial sample only. The content of several elements (U, Mo, etc.) was notably smaller in granulometric fractions, as by processing a sample with H₂O₂, sodium citrate and NaOH it became relatively enriched with these elements or they were carried out from the sample in large quantities. This is also confirmed by the analysis of the dry residue of decanted solutions (Table 4). Consequently, the data obtained show only relative distribution of heavy elements in different grain-size fractions.

**DETERMINATION OF THE MINERAL
COMPOSITION**

The mineral composition of the Dictyonema Shale was determined by X-ray diffractometry. Unoriented preparations were made of ground air-dried samples, mounted into an aluminum sample holder. Oriented preparations were made on a glass slide. For this aim, 10 ml of distilled water was poured into the centrifuge's glass and 2 mg of dry fraction powder was added. After mixing the preparation was left to stay for 24 h. Next, the suspension was processed for 5 min. with the ultrasonic dispersator, pipette onto a glass slide, and dried at room temperature. The major shortcoming of the method is selective sedimentation of particles inside a fraction at the beginning of drying. This effect is not observed in case of narrow fraction limits. Nevertheless, we noted it also in the fraction limits used in our study. In coarser fractions ($\varnothing > 1 \mu\text{m}$) the surface of the preparation was covered with a dark brown film of organic matter. By visual estimations of the colour the film seemed the most intensive in the fraction $\varnothing = 2-5 \mu\text{m}$ and the weakest in the fraction $\varnothing > 5 \mu\text{m}$. In the fraction $\varnothing < 1 \mu\text{m}$ no selective sedimentation of particles was visually detected. Such differentiation is caused by different hydrophilic properties of organic matter and mineral particles.

For identification of clay minerals the preparations

were saturated in ethylene glycol vapour at 60–70°C for 24 h and at room temperature for 12 h. The heat treatment at 250°C and 525°C during 2 h were used.

Diffractograms were prepared by means of the diffractometer DRON-3M, using $\text{CuK}\alpha$ and $\text{FeK}\alpha$ radiation. Scanning step $0,03^\circ 2\theta$ ($\text{Cu K}\alpha$) and counting time 10 and 5 s. in range 2–70 and 2–52° 2θ for unoriented and oriented preparations respectively were used.

Digitally recorded XRD patterns were analyzed with the program AXES (Mändar et al., 1996). To eliminate the influence of possible amorphous components and Lorentz polarization factor, the background line was subtracted from the diffractogram. Background line was drawn manually using a cubic spline. The 2θ corrections were established by quartz in form of a linear equation. The half-width and exact position of a peak were measured by successive approximation of the peak's shape by Gauss, modified Lorentz and Pearson VII functions, applying the Levenberg-Marquardt method.

For the quantitative mineralogical analysis experimental proportionality coefficients, found on the basis of artificial mixtures were used. The coefficients were adjusted for the material studied according to the data of chemical analyses (Table 5). The calculations based on peak heights. The chemical composition of minerals is given in Table 6.

Table 5

THE VALUES USED BY QUANTITATIVE MINERALOGICAL ANALYSIS

Mineral	Quartz	Sanidine	Mica	Illite	Hydroillite	Chlorite	Pyrite	Apatite
Measured peak (Å)	3.34	2.99	10	10	10	14.0 & 7.1	2.71	2.8
Corundum number	4.5	0.54	0.81	0.45	0.315	1.125	1.575	4.05

Table 6

THE NORMATIVE CHEMICAL COMPOSITION OF MINERALS (THE AVERAGE VALUES FROM MANY REFERENCE DATA) USED TO CALCULATE THE CHEMICAL COMPOSITION OF SAMPLES

Component	Content of component in the mineral, %							
	Quartz	Sanidine	Mica	Illite	Hydroillite	Chlorite	Pyrite	Apatite
SiO_2	100	65	45.5	50.1	51.8	25		
TiO_2			0.1	0.2	0.5			
Al_2O_3		18.5	35	30.5	25.3	22		
Fe_2O_3			2.1	3.3	4.5	4		
FeO			0.7	0.7	0.7	23	59.6	
MgO			0.6	1.9	3.4	15		
CaO		0.5	0.3	0.4	0.4			55
Na_2O		0.1	0.1	0.1	0.1			
K_2O		15.9	10.8	6.9	5.8			
P_2O_5								39
H_2O			4.8	6	7.5	11		
S							53.5	
CO_2								3
F								3
Sum	100	100	100	100	100	100	113.1	100

The mineral composition of the initial samples showed no changes after processing with H_2O_2 , sodium citrate and NaOH. Still, in the dry residue of the decanted solution there appeared some new but hardly distinguishable formations. For example, let us consider the results of the X-ray diffractometric analysis of intermediate products of chemical processing of sample 3 from borehole F 328. The dry residue of the decanted solution, got by processing the sample with H_2O_2 , is dominated by $K_2Fe_5Fe_4(SO_4)_{12} \cdot 18H_2O$ (voltaite – ICPDS 20–1388). Additionally, there is at least one component, which remains undetermined. In the dry residue, obtained after processing with sodium citrate, $Na_3C_6H_5O_7 \cdot 2H_2O$ (sodium citrate – ICPDS 16–1170), is predominating. There occur small amounts of two yet undetermined components, one of which is found also in the dry residue of the solution got after processing with H_2O_2 . The dry residue of the solution that remained after processing with NaOH has a complex composition. The main components are $Na_2S \cdot 5H_2O$, $Na_3H(CO_3)_2 \cdot 2H_2O$ and sodium citrate. There occurs also $Na_2Fe_2Si_{0,22}O_{4,44} \cdot 2,8H_2O$ (ICPDS 27–717). Several components are not identifiable. Background lines of diffraction curves show the existence of amorphous phases in all three samples.

CONCLUSIONS

To sum up, we may note that the methodology, which we used to determine the texture and mineral composition, gave reliable, coincident at repeat analyses, data for 126 fractions of the Dictyonema Shale.

The above-described methodology has been used

at studying the geochemical characteristics and formation conditions of the Dictyonema Shale. It can be applied also for studying other strongly consolidated unmetamorphosed argillaceous rocks rich in organic matter.

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