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AUTHIGENIC CARBONATE MINERALS IN THE TREMADOCIAN GRAPTOLITIC ARGILLITE OF ESTONIA

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In the present paper the morphological description, mineralogical and chemical composition of diagenetic carbonate formations occurring in low-grade oil shale, known as Tremadocian graptolitic argillite or Dictyonema shale, is given. The role of these formations in the redistribution of several microelements during diagenesis is discussed. The results obtained permit us to draw some conclusions about the mechanism and time of authigenic minerals formation.

Introduction

The Tremadocian (early Ordovician) graptolitic argillite is distributed in northern Estonia in a longitudinal belt. It reaches a maximum thickness of 7 meters in northwestern Estonia. The thickness decreases from west to east and from north to south (Fig. 1) and, in the same directions, there is an increasing abundance of siltstone interlayers of a few millimeters to some centimeters thick.

These interlayers contain several authigenic minerals which are characteristic of argillite, including sulphides, phosphates, silicon oxides and carbonates.

In the epicontinental marine Tremadocian basin chemogenic or biogenic carbonate sedimentation was nil. The graptolitic argillite contains mostly diagenetic carbonate minerals [1].

Authigenic carbonate minerals have been investigated from the underlying Cambrian [2] and Tremadocian clastic sediments [3, 4].

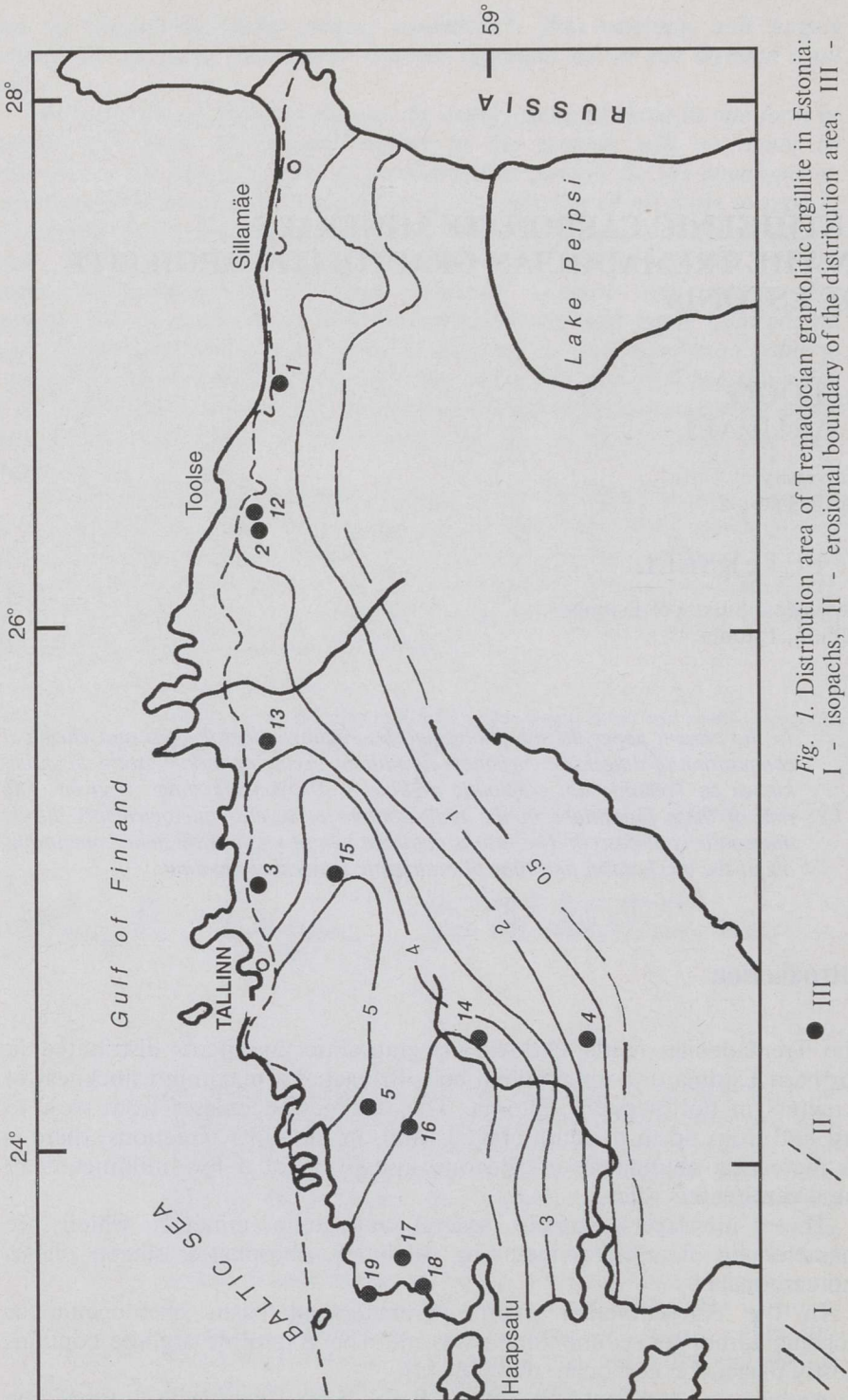


Fig. 1. Distribution area of Tremadocian graptolitic argillite in Estonia:
 I - isopachs, II - erosional boundary of the distribution area, III -
 - boreholes and outcrops

Material and Methods of the Study

During the last decades the authors have studied the occurrence of authigenic carbonates in numerous outcrops and drill cores of graptolitic argillite. The mineralogical composition of these carbonates was determined by optical methods, and by X-ray powder diffractometry in the structural analysis laboratory of the Geological Institute, University of Tartu, using a DRON-3M diffractometer with filtered Fe-K α radiation. Diffractograms were run from 2 to 92°2 θ with a 0.03 step and a counting time of 5 seconds from the samples rotating in their own plane surfaces. The samples were prepared for analysis by grinding the rock to powder in an agate mortar and mounting the powdered samples in aluminium holders. The mineral phases were quantified using corundum numbers (proportionality coefficients) found by the method of artificial mixtures.

The chemical composition of the carbonates and the mode of occurrence of elements in anthraconite concretions were determined from the samples pulverized in the agate mortar; the host rock (i.e. graptolitic argillite) samples, however, were powdered (<0.05 mm) in mechanical cast-iron and ceramic equipment. Afterwards the concretion samples were dissolved by heating them in 3.5 % HCl. The insoluble residue was washed with distilled water and dried. Three fractions were obtained: concretion, insoluble residue and the acid leachate. The samples of these fractions and of the host rock (argillite or siltstone) were analysed in the laboratory of the Geological Survey of Estonia. The methods used and detection limits are presented in Table 1. The reliability of the analyses was confirmed by using standard samples obtained from the Russian Geological Ministry, Scandinavian countries, Denmark and China.

Table 1. Analytical Methods Used in This Study and Their Detection Limits

Detection limits														
%			ppm											
CaO	MgO	Fe ₂ O ₃	Mn	Cd	Cu	Ni	Pb	Zn	Mo	U	V	Ba	Sn	P
Chemical analysis														
100	100	100												
Atomic absorption analysis AAS-F														
			5		2	5	2	2						
Atomic absorption analysis AAS-Gr														
			0.1											
X-ray fluorescence analysis														
					2		2	2						
Semiquantitative spectral analysis														
											3	60	30	600

Results

Carbonate Cement

Carbonate cement occurs mainly in the siltstone interlayers of the graptolitic argillite. Carbonate cementation is sporadic. The terrigenous material is cemented only spot-wise. The strongly carbonate-cemented siltstone contains basic and pore cement. Elsewhere, carbonate cement was noted only at contacts of clasts, i.e. we have to do with contact cement.

The degree of recrystallization of carbonate pore (more rarely basic) cement is variable and may consist of fine-crystalline, poikilitic or crustified types. Fine-crystalline cement is the most abundant. Terrigenous clastic particles are joined by small carbonate crystals of irregular shape, which occur as disordered, more seldom as oriented, clusters.

Poikilitic cement consists of coarse, often well-developed dolomite or calcite crystals, which during growth have incorporated clasts into them. The carbonate crystals are much greater in size than the clasts. Poikilitic cement occurs prominently in the core of the Põõsaspea borehole, where the rock is wholly composed of large rhombohedral calcite crystals. In places clasts are missing and there occurs pure colourless calcite free of admixtures. Interbeds of rather similar bituminous limestone are recorded only in the equivalent Alum Shale of Sweden [5].

Crustified cement is distributed in peripheral parts of more strongly cemented silt patches, where it forms only crusts (rims and cases) around clasts.

Carbonate minerals not only fill the pores between clasts, but often also etch them considerably. This has caused the formation of corrosive cement.

Concretions

Anthraconite concretions form peculiar authigenic carbonate bodies in graptolitic argillite. Naturally these are druses. They form irregular spherulites up to 15 cm in diameter (Fig. 2). There occur also concretions composed of carbonate scalenohedrons that lie vertically on the surface of the carbonate layer in the overlying sediments of the siltstone interbed (Fig. 3). Anthraconite crystals always distort the initial laminated bedding of the host argillite, by forming pressure structures. The anthraconite concretions in the siltstone interlayers always are located as horizontal rows on different levels in the argillite section. They are considerably more numerous in the eastern part of the area of graptolitic argillite. In western Estonia the concretions are mostly found in the southern part of the area, which is also characterized by numerous siltstone interlayers. The areal and vertical distribution of concretions shows no strict regularity.

Anthraconite concretions are composed of carbonate crystals arranged in a bunch-like pattern. The crystals are elongated scalenohedrons with well developed surfaces and edges. The crystals are typically calcite, but

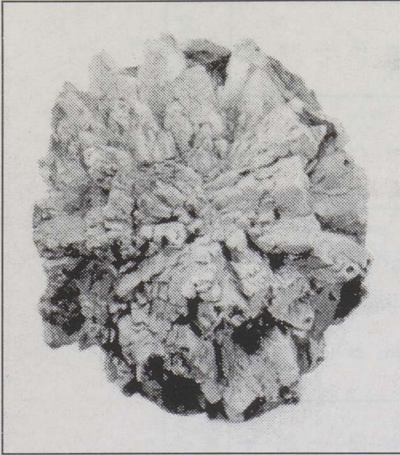


Fig. 2. Spherulite-like anthraconite (1 : 2) concretion (Maardu)



Fig. 3. Anthraconite concretion (1 : 2) (polished section) showing the radial arrangement of crystals (Hiemäe)

where calcite is replaced by dolomite, their scalenohedral shape is preserved. As anthraconite concretions grew in the siltstone interlayers, they incorporated quartz and feldspar grains, clay particles and organic matter. Different amounts of impurities have caused the variation in the colour of crystals from colourless to dark brown.

Mineralogical Composition of Carbonate Material

The percentages of minerals in the siltstone interlayers are variable. Predominating is quartz (up to 70 %). Of the carbonates, the most widespread is calcite (up to 20 %). Dolomite is absent or occurs in small amounts. The content of feldspar and pyrite is as much as 20 %. On the surface of pyrite crystals jarosite and gypsum have formed. Additionally 10 Å micas and hydromicas (illite) were noted.

Dolomite prevails in samples 1 to 4 (Table 2). The main component of anthraconite is either dolomite (84-97 %) or calcite (70-96 %). Accessory minerals include quartz, K-feldspar, apatite, micas, pyrite, gypsum and jarosite (Table 2).

A detailed analysis of the shape of peaks suggests that samples 1 to 3 contain dolomites of a varied chemical composition. These peaks, when they become joined, are asymmetric in shape (104 reflection) or show several maxima (006 reflection) (Fig. 4a,b). The (104) and (006) lattice plane spacing of the possible components and the estimated lattice parameters are presented in Table 3. Also given are the supposed multiplicities of Ca, Mg and Fe cations, which were determined by the linear interpolation method, using the data referenced by R. Y. Reeder [6].

The chemical composition of dolomite is variable. In samples 1 to 4 dolomite predominates. In samples 1 to 3 part of the Mg positions are

Table 2. Mineral Composition of Anthraconite Concretions and Siltstone Interbeds, %

Sample No.	Borehole or outcrop	Depth of occurrence, m	Calcite	Dolomite	Quartz	Orthoclase	Albite	Illite	Apatite	Pyrite	Gypsum	Jarosite
Anthraconite concretions												
1.	Hiiemägi		7	87	1	1	0	0	3	1	0	0
2.	Toolse 797	15.05	2	84	6	2	0	0	4	1	2	0
3.	Maardu		0	96	0	1	0	0	3	0	0	0
4.	Valgu V98	244.0	0	95	1	1	0	0	2	1	1	0
5.	F318	63.6	70	2	9	6	0	5	3	2	2	2
Siltstone												
6.	Toolse 797	15.1	0	0	65	5	0	0	3	21	2	4
7.	F302	37.5	8	0	50	9	0	12	0	16	2	3
8.	F328	101.1	20	0	68	3	0	4	2	2	0	1
9.	F338	102.3	0	0	39	16	2?	18	11	10	0	3
10.	Põõsaspea	49.4	96	0	0	0	0	4	0	0	0	0
Corundum number I/I_c for the ($d = \dots$) reflection			3.38 (3.03Å)	2.93 (2.89Å)	4.50 (3.34Å)	1.58 (3.24Å)	2.52 (3.19Å)	0.45 (10Å)	1.17 (2.79Å)	1.58 (1.63Å)	2.34 (7.61Å)	0.9 (5.09Å)

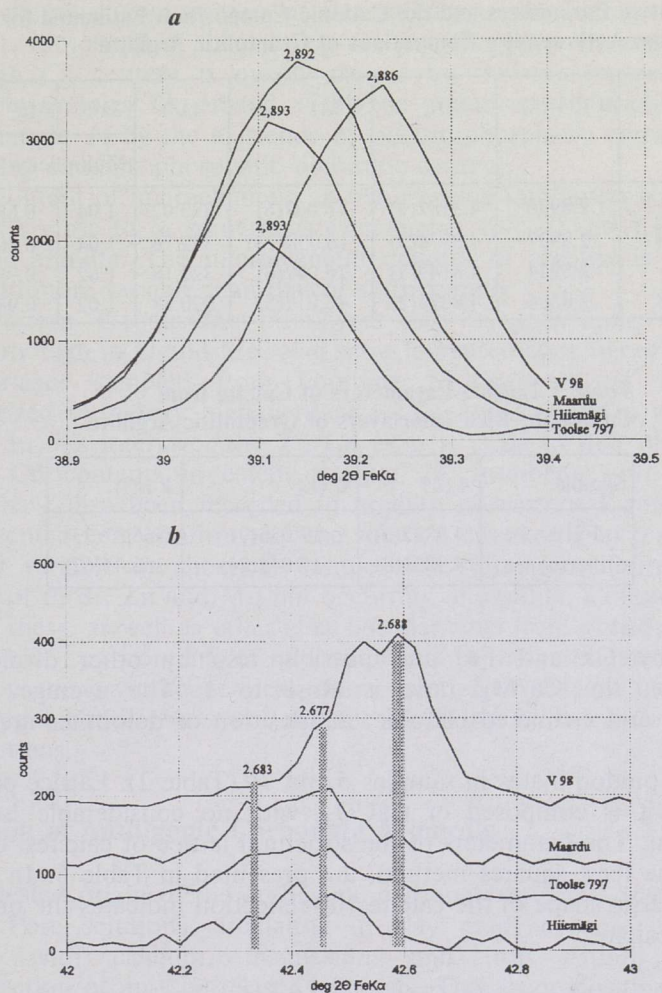


Fig. 4. Location of dolomite (a) (104) reflection and (b) (006) reflection for the samples 1 (Hiemägi), 2 (Toolse 797), 3 (Maardu) and 4 (Valgu98)

Table 3. Lattice Parameters and the Cationic Composition Estimated for Dolomite from Anthraconite Concretions of Graptolitic Argillite

Dolomite variety	d 104 (Å)	d 006 (Å)	A (Å)	C (Å)	V (Å ³)	Ca ²⁺	Mg ²⁺	Fe ²⁺
						Multiplicity		
D1	2.886	2.668	4.807	16.012	320	1	0.96	0.04
D2	2.893	2.678	4.815	16.067	323	1.04	0.72	0.24
D3	2.898	2.683	4.820	16.101	324	1.06	0.56	0.38

Table 4. Lattice Parameters and the Cationic Composition Estimated for Typical Dolomite from Anthraconite Concretions of Graptolitic Argillite

Sample	d 104 (Å)	A (Å)	C (Å)	V (Å ³)	Ca ²⁺	Mg ²⁺	Fe ²⁺
					Multiplicity		
1. Hiimägi	2.8930	4.8182(2)	16.067(6)	323.02	1.04	0.68	0.28
2. Toolse 797	2.8927	4.8176(5)	16.058(13)	322.76	1.04	0.70	0.26
3. Maardu	2.8924	4.8149(2)	16.047(6)	322.18	1.02	0.78	0.20
4. Valgu V98	2.8866	4.8074(2)	16.017(5)	320.58	1.02	0.96	0.04

Table 5. Lattice Parameters of Calcite from Carbonate-Rich Interlayers of Graptolitic Argillite

Sample	A (Å)	C (Å)	V (Å ³)
5. F318	4.9832(3)	17.036(9)	366.37(23)
6. Põõsaspea	4.9831(8)	17.042(24)	366.47(62)

occupied by Ca and Fe, and possibly also by other divalent ions. In sample 4, the Ca/Mg ratio is close to 1. The average structural parameters and estimated cationic composition of dolomites are given in Table 4.

Calcite predominates in samples 5 and 10 (Table 2). Lattice parameters show that it is composed of CaCO₃, with no considerable isomorphic replacement. The parameters of the structural lattice of calcites, calculated by using the least-squares method, are presented in Table 5. In sample 5 the asymmetric shape of the calcite 104 reflection indicates the presence of some Mg-calcite.

Chemical Composition of the Carbonate Material

The initial calcitic composition characterizing anthraconites may be seen only in drill core from borehole F-318, where the host rock is also very rich in calcite. In the other samples calcite has been replaced by dolomite. The chemical composition of these concretions is similar and is characteristically high in Mg, Fe and Mn contents.

The content of microelements in anthraconite is rather monotonous. No great deviations were observed from the predominating one (Table 6). Comparing the contents of microelements recorded for anthraconite with those detected in the host rock - argillite, we can note a specific pattern: the content of Cu, Ni, Pb and some other microelements is considerably lower in the crystals of calcitic and dolomitic anthraconite than in the host rock. For Cd and Mn, however, the reverse tendency is observed. This relation, nor the concentration of Sr which frequently co-occurs with carbonates, has not been much affected by the dolomitization of anthraconite. Quite obviously there was no concentration of microelements in authigenic carbonate minerals during diagenesis.

The chemical composition of the carbonate silt interlayers is varied (Table 6). Almost all of these layers are rich in pyrite. In samples 16 and 19 a high Ca content is mostly caused by the occurrence of calcitic cement, in samples 11, 12 and 17 by the presence of phosphatic cement and in sample 14 by the existence of calcitic-phosphatic cement. Sample 18 probably contains phosphatic-dolomitic cement.

The content of microelements in the siltstone interlayers is also varied. It is rather close to or sometimes even higher (Ni, U, etc.) than that of graptolitic argillite. The microelement content of argillite is prevalingly higher and more variable than that of anthraconite.

In western Estonia the interlayers rich in phosphatic cement are particularly high in U and Mo, also show increased contents of Ni and Ba. An interlayer sampled from borehole M-46 south of Maardu, is characterized by a very high content of Zn and Cd and a very low Ni content. In this interlayer the Zn/Cd ratio is close to that of anomalous Zn and Cd contents in calcite sample 20. Interbeds with a high Zn content have also been recorded in argillite in western Estonia [7]. The data presented here confirm that the solution circulating in the interlayers was very variable in chemical composition, often containing abundant amounts of P, Sr, Zn and Mn not occurring in argillite. Consequently, the influx of these, as well as other (Fe, Ni) elements from outside the system was possible. Low contents of microelements in the carbonate samples are caused by the crystallochemical characteristics of calcite and dolomite. Their crystal lattices were not capable of taking up microelements from pore solutions.

Formation of Authigenic Carbonate Minerals

The suggested origin of the authigenic carbonate minerals was possibly as follows. Pore solutions circulating in clay muds became continuously enriched with calcium, magnesium and iron cations from the decomposition of unstable clastic minerals. The decomposition of organic matter caused the increase of the CO₂ content in the pore solutions. The calcium entering the solution formed soluble calcium bicarbonate Ca(HCO₃)₂, which also remained in solution. The waters with bicarbonate were expelled into coarser more porous silt interlayers by the compaction of clays. At the same time, ammonium ion (NH₄) formed during the decomposition of the organic matter buried in sediment strongly increased the alkalinity of the pore waters and pH. The removal of carbon dioxide from the pore waters by the compaction of muds and the increased pH caused the decomposition of calcium bicarbonate.

Clay particles and organic colloids in contact with the pore solutions of the siltstone interlayers served as crystallization centres that brought about the simultaneous precipitation of many small carbonate crystals. In this way fine-crystalline basic or pore cement was formed. Such carbonate cement was developed only in places. The change of the ratio of the masses of crystallizing calcite and fine-dispersed admixture in the pore solutions caused the formation of crustified carbonate cement.

Table 6. Chemical Composition of Carbonates and Graptolitic Argillite

Sample No.	Station	Depth, m	CaO	MgO	Fe ₂ O ₃	Mn	Cd	Cu
			%			ppm		
Anthraconite concretions								
1.	Outcr. Hiimägi		30.54	17.42	2.12	2190	1.30	7
2.	B.h. Toolse 797	15.1	25.74	15.63	4.98	2480	0.96	21
3.	Maardu pit		28.35	17.20	3.94	2080	1.07	15
4.	B.h. V-98	244.0	27.48	18.49	2.32	882	1.02	22
5.	B.h. F-318	63.6	43.06	0.96	2.41	4080	1.46	34
Acid leachate (3.5 % HCl) of anthraconite concretions heated to 100 °C								
1.	Outcr. Hiimägi		18.98	10.15	0.87	1500	0.92	4
2.	B.h. Toolse 797	15.1	18.16	10.54	1.88	1890	0.69	4
3.	Maardu pit		18.69	10.70	1.32	1430	0.63	8
4.	B.h. V-98	244.0	14.42	9.31	0.40	357	0.55	3
5.	B.h. F-318	63.6	30.01	0.37	0.35	1780	0.95	5
Insoluble residue of anthraconite concretions								
1.	Outcr. Hiimägi		11.46	6.97	1.26	660	0.38	6
2.	B.h. Toolse 797	15.1	7.13	4.62	2.83	600	0.27	18
3.	Maardu pit		9.44	6.20	2.48	630	0.44	12
4.	B.h. V-98	244.0	12.62	8.62	1.48	230	0.47	19
5.	B.h. F-318	63.6	12.76	0.39	1.54	1470	0.51	27
Host rock (argillite) of anthraconite concretions								
6.	Outcr. Hiimägi		0.54	1.06	4.16	106	0.22	131
7.	B.h. Toolse 797	15.1	0.96	0.80	5.91	119	0.31	121
8.	Maardu pit		1.10	0.90	6.00	119	0.38	124
9.	B.h. V-98	244.0	1.03	1.29	4.94	132	0.40	131
10.	B.h. F-318	63.6	6.16	1.01	5.28	758	0.26	69
Siltstone interlayers in argillite								
11.	B.h. Toolse 797	15.1	2.53	0.07	15.00	170	0.29	55
12.	B.h. Toolse 811	14.7	5.97	0.55	15.80	451	0.29	124
13.	B.h. M-46	31.8	1.40	0.38	10.04	50	74.40	231
14.	B.h. F-302	130.9	8.60	0.24	12.16	734	0.26	72
15.	B.h. F-284	78.3	0.70	0.05	50.74	50	0.74	194
16.	B.h. F-328	101.1	12.34	0.05	3.18	771	0.51	38
17.	B.h. F-338	102.3	7.20	0.41	7.48	324	0.40	195
18.	B.h. F-339	92.5	7.08	2.70	7.74	707	0.54	176
19.	B.h. Põõsaspea	49.4	36.21	0.45	7.25	4527	1.01	29
Among this calcite		49.4	49.43	0.17	1.23	3340	2.85	18

During later diagenesis, the amount of finely dispersed particles in the pore solutions decreased greatly and a typically poikilitic carbonate structure was developed. During their growth, large dolomite crystals were included into them as well as clasts from the host rock. During late diagenesis and also at earlier stages the impact of carbonates on clast grains became aggressive and corrosive cement was formed.

In the silt interlayers the growth of carbonate concretions took place and it continued until the ammonium ions ceased to appear or the surrounding sediment became totally void of dissolved carbonate material.

Table 6. Chemical Composition of Carbonates and Graptolitic Argillite (end)

Sample No.	Ni	Pb	Zn	Mo	U	V	Ba	Sr	P
ppm									
Anthraconite concretions									
1.	29	40	5	2.3	17	80	< 60	60	< 600
2.	76	65	6	17	32	100	100	80	1000
3.	33	40	5	6.8	16	200	60	80	< 600
4.	47	45	5	49	22	150	60	60	< 600
5.	76	53	13	10	20	100	100	100	< 600
Acid leachate (3.5 % HCl) of anthraconite concretions heated to 100 °C									
1.	13	20	5						
2.	23	25	5						
3.	15	25	4						
4.	14	13	3						
5.	24	18	3						
Insoluble residue of anthraconite concretions									
1.	14	16	< 2						
2.	50	30	< 2						
3.	22	16	< 2						
4.	28	18	< 2						
5.	41	23	3						
Host rock (argillite) of anthraconite concretions									
6.	417	99	68	844	479	1500	350	30	< 600
7.	283	156	36	106	101	1000	350	80	1000
8.	211	203	35	213	120	1000	350	80	1800
9.	222	124	45	1539	173	1000	500	80	1500
10	77	98	37	64	62	600	400	80	600
Siltstone interlayers in argillite									
11.	228	170	< 2	35	47	30	200	80	2970
12.	267	199	18	82	26	40	100	400	10,300
13.	48	104	10,640	47	14	150	300	80	2750
14.	378	135	7	44	84	100	250	100	5420
15.	778	190	21	80	< 40	25	60	< 40	< 600
16.	89	54	27	161	34	60	100	80	2970
17.	444	195	13	708	466	400	500	300	23,910
18.	394	111	42	408	204	400	350	150	7820
19.	161	51	150	49	64	150	150	100	600
Among this calcite	47	45	335	22	27	100	60	100	< 600

The growth of radial calcite aggregates resulted in the deformation of the soft and still plastic interbeds of clay and silt. The bed- and pocket-shaped siliceous rocks which had developed during earlier phases of diagenesis, were deformed and typical diagenetic pressure structures were formed.

Mg isomorphically replaced Ca in the calcite crystals formed during late diagenesis as well as during catagenesis over a very long period. Such replacement was first of all caused by an increasing Mg/Ca ratio in the circulating pore waters, characterised by an increase in biogenic Mg ions

released by the decomposition of clastic minerals and organic matter and by opal desorption in earlier formed siliceous layers. In tectonic dislocation zones of northeast Estonia the influx of Ca and Mg ions from the overlying Lower Ordovician limestones could take place [8]. This accounts for the distribution of catagenic dolomite cement in silt interlayers in the immediate vicinity of tectonic dislocation zones.

One reason for dolomitization could also have been the influx of material from deep subsurface layers [9].

Summary

Authigenic carbonates in Tremadocian graptolitic argillites are mostly related to siltstone interbeds. Carbonate minerals form cement or concretions.

Siltstone interbeds contain predominantly carbonate basic or pore cement. According to the degree of recrystallization of carbonate cement, we may distinguish the fine-crystalline, poikilitic or crustified types. The mineralogical composition of cement is variable. In the western part of the outcrop area, the cement is represented by calcite and in the eastern part by dolomite as well. These interbeds are also characterized by phosphatic cement and even by fragments of an earlier formed chemogenic phosphate layer (borehole Toolse 811).

Peculiar authigenic formations are druse-like anthraconite concretions, which during growth have incorporated clasts and disturbed the initial bedding of argillite. Concretions are formed by typical scalenohedral crystals of calcite.

The calcite crystals formed during diagenesis show isomorphic replacement of Ca by Mg during late diagenesis as well during catagenesis.

The content of microelements in the carbonates is considerably smaller than in the host rock.

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