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GEOCHEMISTRY OF MAJOR ELEMENTS IN MIDDLE ORDOVICIAN CARBONATE ROCKS: COMPARATIVE ANALYSIS OF ALTERATION ZONES, NORTH ESTONIA

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Abstract. Altered and/or mineralized bodies formed due to secondary processes occur frequently in the early Palaeozoic carbonate deposits in Estonia. Selectively dissolved and leached rocks, karst cavities, metasomatic dolomite beds, and fracture-related unconformable bodies, calcite, sulphide, sulphate, and oxide minerals filling pore space (fractures, fissures, and caverns) are the most common phenomena. In the Middle Ordovician there were studied four alteration zones: three in limestones of the Väo Formation from the Väo and Harku outcrops, and one in the Viivikonna Formation from the Narva opencast. The content of 12 oxides (CaO, MgO, FeO, Fe_2O_3, K_2O, Na_2O, SiO_2, Al_2O_3, TiO_2, P_2O_5, SO_3, and CO_2) in the sampled rocks was determined by the classical wet-silicate analysis and interpreted using the correlation analysis. Two geochemical types of dolomitization, and correspondingly two groups of rocks, can be defined considering the distribution of CaO, MgO, total iron, Fe^{2+} and Fe^{3+}, and sulphur. The first group consists of background rocks almost untouched by dolomitization and those from the Väo Formation, which occur close to the fractures in the Harku outcrop (MgO concentration up to 4%, CaO 42—52%). The second clearly defined group comprises the almost fully dolomitized rocks of the Viivikonna Formation of the Narva opencast (MgO concentration in these rocks is about 14—18%, CaO makes 30%). In the Väo outcrop and Narva opencast the FeO concentration is in positive correlation with that of MgO. The results obtained are compared with the earlier studies of different authors.

Key words: alteration, dolomitization, fractures, carbonate rocks, chemical composition, correlation analysis, carbonate—sulphide mineralization, unconformities, Ordovician, Estonia.

INTRODUCTION

This study serves as the first stage in the complex petrophysical and geochemical investigation of early Palaeozoic carbonate rocks of Estonia. Below the chemical composition of rocks in the alteration zones is discussed and an attempt is made to classify altered rocks by geochemical data. Altered and/or mineralized bodies of distinct geological setting, caused by different-age secondary processes, are often found in the early Palaeozoic carbonate rocks in Estonia. Altered rocks are represented by metasomatic dolomite beds and fault-(fissure-) related unconformable dolomite bodies. Most commonly these are characterized by selectively dissolved and leached rocks, karst cavities, calcite, sulphide, sulphate, and oxide minerals filling pore space (fissures and caverns).

Samples for the study were taken from two vertical fracture-related dolomitization and mineralization zones in the limestones of the Väo Formation from the Väo outcrop and from a wide dolomitized zone of the same formation in the Harku outcrop. In the Narva opencast, a laterally extended leached and dolomitized body occurring beneath the Ordovician—Devonian unconformity in the limestones and kukersite oil shale of the Viivikonna Formation was sampled.

The concentration of 12 oxides (CaO, MgO, FeO, Fe_2O_3, K_2O, Na_2O, SiO_2, Al_2O_3, TiO_2, P_2O_5, SO_3, and CO_2) in the rocks was determined by the classical wet-silicate analysis. The distribution of elements showed that the variation of the CaO, MgO, FeO, Fe_2O_3, and SO_3 concentration was definitely controlled by secondary processes. Changes in the content of other oxides in the rocks were mainly connected with the occurrence of various argillaceous admixtures, which indirectly influence the intensity of secondary processes. Using the correlation analysis, at least two different types of secondary altered carbonate rocks were revealed. Besides CaO and MgO substitutions, these are characterized by different relationships of total iron, Fe^{2+} and Fe^{3+}, and sulphur. The fissure-filling calcite—sulphide mineralization has its own specific characteristics.

GEOLOGICAL SETTING

Since the beginning of the Palaeozoic, the territory of northern Estonia has been among the most stable areas of the East European platform subjected to very weak epeirogenic movements (Сувейдзис, 1979). On the territory of Estonia the Ordovician sequence is represented by shallow-water open shelf carbonate rocks ranging from 70 to 180 m in thickness (Männil, 1990). The uniform homocline structure of the Ordovician—Silurian carbonate complex is gently sloping (usually 2.9—4.4 m/km) to the south. Systems of faults and fractures complicating the homocline structure were formed in the studied region mainly due to the Palaeozoic tectonic processes taking place in the surrounding areas. Along these fracture systems, crosscutting both aquifers and aquitards, there occurred migration of fluids (deep and superficial) responsible for alteration and mineralization of deposits.

Altered and mineralized bodies have been described in the early Palaeozoic carbonate rocks from different localities (Möls, 1961; Вахер et al., 1962; Газизов, 1971; Pichugin et al., 1978; Вингисаар & Таалманн, 1974; Niin et al., 1981; Шогенова & Туулинг, 1990). In Silurian and Ordovician deposits there occur bodies of cavernous dolomites and limestones of various sizes formed through alteration of rocks. The altered rock bodies are commonly directed either vertically or horizontally due to tectonic (faults, fracture zones, fissures) or stratigraphical (unconformities, distinct beds) control, respectively. Selective solution and leaching of carbonate minerals and/or metasomatic substitution of MgO for CaO are the main evidences of zonal alteration processes. Secondary dolomite replaces sedimentary calcite (including fossil debris) in rocks. Secondary calcite fills the pore space (fissures, caverns) together with different iron sulphide, sulphate, oxide, and hydroxide minerals. Increased porosity, changes in colour and mineralization are the main observable macroscopic evidences of secondary processes. Fresh water infiltration and karst processes occurring at different times (from the early Palaeozoic to Holocene), and late Palaeozoic telethermal metasomatic dolomitization have been supposed as probable causes of alteration/mineralization, although there are cases of genetically unidentified dolomitization and leaching (Möls, 1961; Вахер et al., 1962; Газизов, 1971; Pichugin et al., 1978; Niin et al., 1981; Кийпли et al., 1984).

In the Ordovician and Silurian rocks of northern Estonia there prevail fairly pure detrital limestones. Based on geochemical studies, four types of Lower Palaeozoic sedimentary carbonate rocks were revealed by Kiipli et al. (Кийпли et al., 1984), three of which included dolomitized rocks. The first type was sampled and described from an areally dolomitized layer corresponding to the Pae Member of the Väo Formation. This layer has been studied earlier by different authors and described in detail by Kiipli (Кийпли, 1983a). In northern Estonia the Pae Member is represented by a distinct 0.2—0.6-m-thick dolomite layer extending from west to east for over 200 km.

The second type of secondary dolomites occurs in the Middle and Upper Ordovician (reaching also the Silurian in central Estonia) close to the erosional contact with Devonian carbonate and clastic or mixed deposits forming in large scale an unconformable body beneath the Devonian unconformity surface. The mineralogical composition of these rocks was studied in detail by Kleesment (Клеесмент et al., 1980).

The third type associated with tectonic disturbances is related to fracture zones (Вахер et al., 1962; Pichugin et al., 1978). Large zones of tectonic fracturing and dolomitization occur usually in the areas of both major and minor tectonic disturbances of NE, NS, and NW direction. The NE oriented zones are often discovered and described in NE Estonia (Газизов, 1958, 1971; Вахер et al., 1962; Пуура et al., 1987; Шогенова & Туулинг, 1990).

The fourth type is related to separate fractures, which are often (mostly the NE oriented ones) filled by mineralization (Möls, 1961; Niin et al., 1981; Кийпли, 1983a). In the vicinity of Tallinn and in western Estonia, mineralization of fissures and fractures in limestones occurs with or without dolomitization of wall rocks.

Two groups of dolomites were distinguished based on their genesis: those formed during sedimentation processes and as a result of secondary alteration processes. The last type may be subdivided into early diagenetic and late diagenetic varieties (Russian term — catagenetic).

In the present study, which is a part of larger research, we tried to determine the geochemical signatures of different types of Lower Palaeozoic carbonate rocks by means of statistical correlation analysis. The study and comparison of the composition of altered and unaltered rocks in the local zones of disturbances is one way to classify and identify the carbonate rocks of complicated genesis.

RESULTS

Four different types of dolomitized bodies were sampled. The sampling scheme is given in Figs. 1—3. Two thin altered rock zones (Fig. 1*A*, *B*) in fracture walls represent two varieties of fissure fillings in the Väo Formation (including a 0.6-m-thick dolomite layer of the Pae Member): (1) an almost empty NW oriented fracture in SE wall (with only occasional spots of iron oxides, Fig. 1*A*); (2) a NE fissure in the south wall (with calcite—sulphide mineralization, Fig. 1*B*), both in Väo quarry. The third zone is a vertical body in the Väo and Aseri formations, about 50 m wide, occurring in a monoclinal fold (felxure) disturbed by fissures in an artificial channel at Harku (Fig. 2). The fourth zone is an extensive horizontal body, about 1—5 m thick, occurring in the Viivikonna Formation under the Ordovician—Devonian contact in the Narva oil shale opencast (Fig. 3).

Väo quarry

In the quarry the lower and middle parts of the Väo Formation (Rebala and Pae members and the lower part of the Kostivere Member) are exposed in a thickness of 5.8 m. The lower Rebala and upper Kostivere members are characterized by hard grey limestones. The 0.6-m-thick Pae Member is represented by a dark grey porous dolomitized carbonate layer (Fig. 1*A*, *B*). The two alteration zones studied are associated with vertical fractures crosscutting the whole sequence, the Pae dolomite included, and representing regional NE and NW fracture systems. Dolomitization, recrystallization, red-brown colour of rocks, and mineral filling are clearly observable in quarry walls. In the NW oriented fracture zone (Fig. 1*A*) only iron hydroxides were detected in the fracture walls. The richest mineralization was registered in a 3—10-cm-thick vertical NE directed fracture in the south wall (Fig. 1*B*), constituting one in the net of similar veins. Samples were collected from the central mineralization zone, from rocks close to the fractured wall, and unaltered background rocks (at a distance of 1.5—2 m from the fracture).

The chemical analysis showed that, taking the purest unaltered Väo limestone as a reference field ($<1\%$ MgO), a high MgO content in the Pae dolomite occurred only at some distance from the NE oriented fracture (Table, Figs. 1*B*, 4). Consequently, the same process as described by Kiipli (Кийпли, 1983a) appeared to be present near the NE fracture studied.

In the Rebala and Kostivere members, the dolomitization process in the fracture walls was of rather low intensity and inconstant (Fig. 4). In the empty NW fracture wall, in the primary limestones of the Rebala Member, the MgO concentration was 4—15%; 2 m from the fracture it is about 3—8%. In the upper Kostivere Member the wall is not dolomitized. Both in the Pae dolomite layer and fractured walls of Väo quarry, the FeO and MgO concentrations show positive correlation (Fig. 5*B*). Between the FeO and SO_3 concentrations no correlation was established there. The absence of sulphides in the fracture-related dolomites in NE Estonia was noted earlier by Pichugin et al. (1978). Obviously, FeO is incorporated into the dolomite crystals, thus pointing to the reductional environments of dolomitization. Red- and brown-coloured rocks near the fractures, especially in the lower part of the Väo section studied, probably contain Fe_2O_3 in the form of hydroxides (Fig. 4*D*). The calcite—sulphide vein, filling the fracture, consists of pure calcite and iron sulphide.

Harku outcrop

In the artificial channel at Harku the Väo Formation is exposed in incomplete thickness of about 4.5 m. The width of the vertical dolomitization zone is about 50 m. The samples were collected from near the surface of the double disc up to the upper border of the Aseri Formation (Fig. 2). In the central part of the zone, the concentration of MgO changes from 14 to 18% (Table, Fig. 4*B*) and, consequently, the dolomite content reaches 60—80%. Samples of visually unaltered rocks in the outer part of the tectonic zone have the MgO concentration up to 2—5%. The FeO content is higher than in unaltered rocks of the Väo outcrop and varies in the limits of 0.7—1.3%. Unlike the Väo site, the FeO concentration in dolomites of Harku channel depends neither on the MgO nor on the SO_3 concentration (Figs. 5*B*, *C*), although the SO_3 content is usually higher at Harku (Fig. 4*E*). The concentration of Fe_2O_3 is very low in both unaltered and dolomitized rocks. Iron hydroxides are

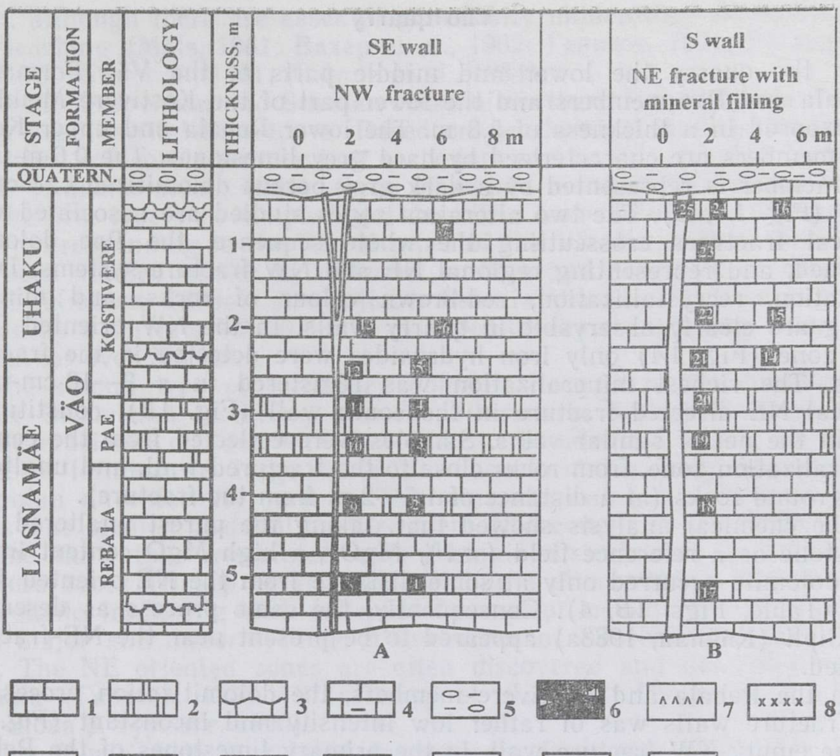


Fig. 1. Section of the Väo Formation in Väo quarry. *A*, sampling scheme of the northwest fracture in the southeast wall; *B*, sampling scheme of the northeast fracture in the south wall.

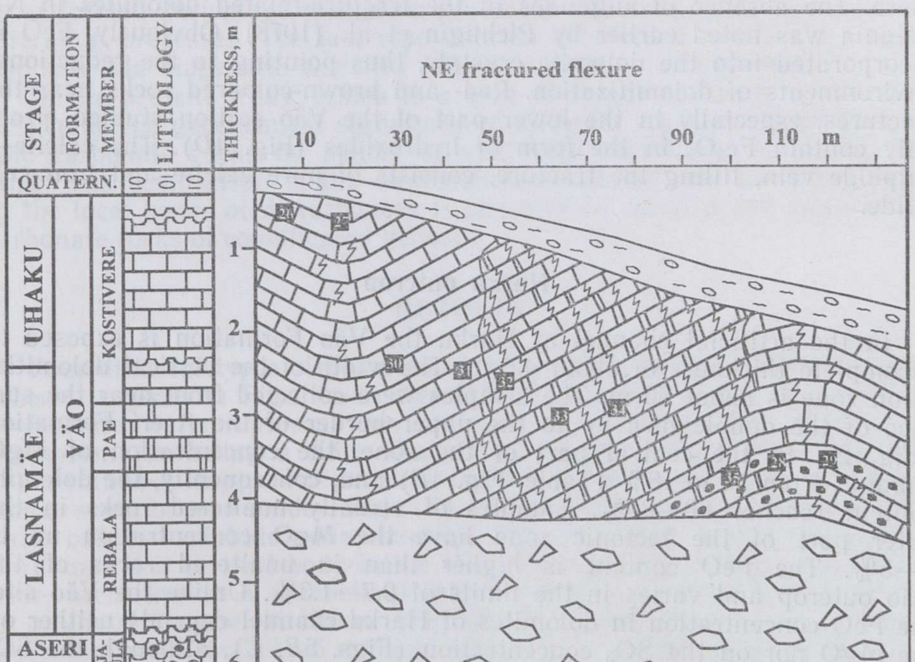


Fig. 2. Section and sampling scheme of the Väo Formation in Harku artificial channel.

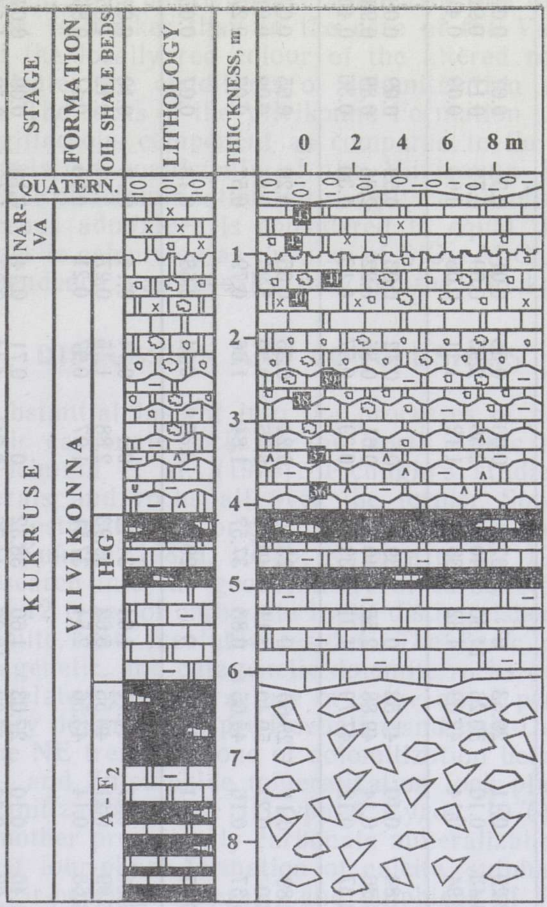


Fig. 3. Section and sampling scheme of the Kukruse Formation in the Narva oil shale opencast.

Legend for Figs. 1—3:
1, limestones; *2*, dolomites; *3*, lumpy limestone; *4*, slightly argillaceous limestone; *5*, Quaternary deposits; *6*, kukersite; *7*, admixture of kukersite; *8*, red-brown rocks; *9*, cavernosity; *10*, fracturing; *11*, discontinuity; *12*, fissure; *13*, iron oolites; *14*, spoil; *15*, sampling points.

met only locally independently of the dolomitization degree (Fig. 5*C*). This enables us to conclude that high FeO values are related to its incorporation into the dolomite crystals as described in the case of Aluvere quarry by Pichugin et al. (1978).

Narva outcrop

In the Narva opencast a laterally extended leached and dolomitized body composed of variably argillaceous limestones and kukersite oil shales was studied below the Ordovician—Devonian unconformity. The section was sampled at the topmost part of the Viivikonna Formation (Kukruse Stage, Fig. 3). The MgO concentration varies between 11—18% corresponding to the content of mineral dolomite of about 50—80% (Fig. 4). Close to the Ordovician—Devonian contact, the rocks are partly red-coloured. The total concentration of iron in this section is stable (0.7—1.9%) (Table, Fig. 4*D*). The main part of iron occurs in the form of

Composition of carbonate rocks in the studied outcrops

Outcrop	Place	Zone	Sample number	Oxide, %	SiO_2	Al_2O_3	TiO_2	CaO	MgO	CO_2	Fe_2O_3	FeO	SO_3	K_2O	Na_2O	P_2O_5
VÄO	SE wall, NW fracture	Reference	1—7	min	2.58	3.17	0.10	29.65	0	39.47	0	0.35	0.01	0.37	0.06	0.10
				max	5.88	4.82	0.19	49.75	15.70	41.41	0.39	2.87	0.19	0.88	0.09	0.81
				avg	4.34	3.98	0.13	43.14	4.99	40.36	0.17	1.21	0.10	0.58	0.08	0.25
		Alteration	8—13	min	3.78	3.29	0.11	29.63	0	37.93	0.03	0.36	0.01	0.51	0.07	0.09
				max	5.57	4.43	0.16	50.26	14.60	40.60	2.36	2.95	0.09	0.72	0.14	0.91
				avg	4.68	3.94	0.14	42.69	4.82	39.49	1.12	1.11	0.05	0.63	0.09	0.41
	S wall, NE fracture with mineral filling	Reference	14—16	min	3.58	1.84	0.10	45.58	0	39.32	0	0.42	0.03	0.52	0.09	0.08
				max	5.32	4.26	0.14	49.88	2.55	40.78	0.61	0.85	0.22	2.86	0.89	0.94
				avg	4.53	3.37	0.12	47.79	1.01	39.91	0.39	0.57	0.13	1.30	0.36	0.40
		Alteration	17—24	min	1.56	0.89	0.11	29.66	0	23.15	0.24	0.35	0.05	0.20	0.05	0.07
				max	8.90	16.0	0.22	50.40	3.11	40.72	8.46	9.30	5.25	0.84	0.09	0.61
				avg	4.86	5.37	0.16	45.65	0.83	37.57	1.84	1.66	0.79	0.57	0.07	0.27
		Mineralization	25		1.38	9.07	0.11	36.26	0	29.64	13.30	0.51	3.68	0.18	0.07	0.05
HARKU	south wall	Reference	26—29	min	5.02	1.86	0.07	40.71	1.04	34.43	0	0.74	0.14	0.78	0.10	0.07
				max	8.77	6.99	0.21	46.55	5.69	39.93	2.88	1.15	0.27	1.18	0.12	1.65
				avg	6.62	4.68	0.14	43.56	2.54	37.51	1.07	0.97	0.21	0.95	0.11	0.85
		Alteration	30—35	min	1.10	1.46	0.10	27.03	1.60	38.32	0	0.71	0.14	0.18	0.09	0.04
				max	8.79	7.08	0.23	47.02	18.20	44.76	0.54	4.44	0.23	1.48	0.12	1.97
				avg	5.48	4.0	0.13	33.80	11.60	40.73	0.19	1.53	0.19	0.76	0.11	0.43
NARVA		Alteration	36—43	min	2.83	3.27	0.12	21.59	11.20	33.49	0	0.73	0.10	0.42	0.08	0.07
				max	1.97	7.03	0.22	28.79	17.60	43.02	0.23	1.86	0.22	1.76	0.12	0.24
				avg	10.20	4.98	0.16	26.16	15.40	38.62	0.03	1.44	0.16	1.20	0.10	0.12

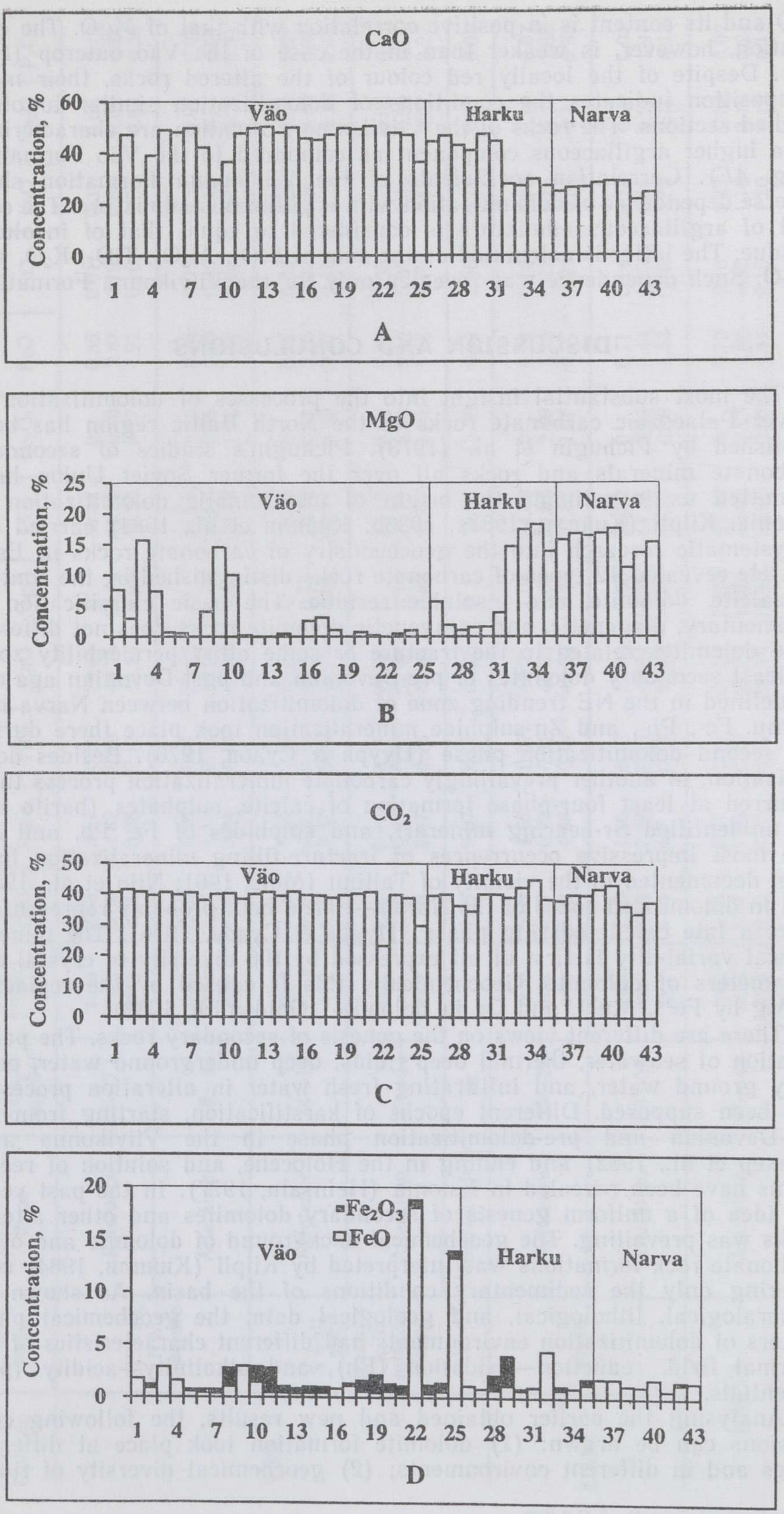
FeO and its content is in positive correlation with that of MgO. The correlation, however, is weaker than in the case of the Väo outcrop (Fig. 5*B*). Despite of the locally red colour of the altered rocks, their main composition indicates the conditions of dolomitization similar to other studied sections. The rocks of the Viivikonna Formation are characterized by a higher argillaceous component as compared to the Väo Formation (Fig. 4*F*). Correlation coefficients of the Viivikonna Formation show inverse dependence of dolomitization with argillaceous admixture. The content of argillaceous admixture is considered to equal that of insoluble residue. The latter is calculated as the sum of SiO_2, Al_2O_3, TiO_2, K_2O, and Na_2O. Such dependence was revealed only for the Viivikonna Formation.

DISCUSSION AND CONCLUSIONS

The most substantial insight into the processes of dolomitization of Lower Palaeozoic carbonate rocks in the North Baltic region has been published by Pichugin et al. (1978). Pichugin's studies of secondary carbonate minerals and rocks all over the former Soviet Union have permitted us to estimate the origin of metasomatic dolomitization in Estonia. Kiipli (Кийпли, 1983a, 1983b; Кийпли et al., 1984) carried out a systematic research into the geochemistry of carbonate rocks in Estonia. He revealed 12 types of carbonate rocks distinguished by the content of calcite, dolomite, and insoluble residue. The basic classification of sedimentary, diagenetic, and catagenetic dolomite rocks does not differentiate dolomites related to the fracture or some other permeability zone. At least secondary dolomites of pre-Devonian and post-Devonian age can be defined in the NE trending zone of dolomitization between Narva and Pärnu. Fe-, Pb-, and Zn-sulphide mineralization took place there during the second dolomitization phase (Пуура & Судов, 1976). Besides dolomitization, in another prevailingly carbonate mineralization process there occurred at least four-phase formation of calcite, sulphates (barite and an unidentified Sr-bearing mineral), and sulphides of Fe, Pb, and Zn. The most impressive occurrences of fracture-filling mineralization have been documented in the vicinity of Tallinn (Möls, 1961; Niin et al., 1981) and in dolomitized zones of the Narva—Pärnu belt, probably representing there a late calcite-bearing phase (Пуура & Судов, 1976). The mineralogical variability is first of all expressed by the diversity of crystal cell parameters of dolomite. Geochemically this is caused by the replacing of Mg by Fe^{2+}, Mn^{2+}, and Ca in dolomite (Goldsmith, 1983).

There are different views on the genesis of secondary rocks. The participation of seawater, thermal deep fluids, deep underground water, ordinary ground water, and infiltrating fresh water in alteration processes has been supposed. Different epochs of karstification, starting from the pre-Devonian and pre-dolomitization phase in the Viivikonna area (Вахер et al., 1962) and ending in the Holocene, and solution of recent forms have been revealed in Estonia (Heinsalu, 1977). In the past years the idea of a uniform genesis of secondary dolomites and other altered rocks was prevailing. The geochemical background of dolomite and other carbonate rock formations was interpreted by Kiipli (Кийпли, 1984) considering only the sedimentary conditions of the basin. As shown by mineralogical, lithological, and geological data, the geochemical parameters of dolomitization environments had different characteristics of the thermal field, reduction—oxidation (Eh), and alkalinity—acidity (pH) potentials.

Analysing the earlier obtained and new results, the following conclusions can be drawn: (1) dolomite formation took place at different times and in different environments; (2) geochemical diversity of fluids


CaO
Concentration, %
60
40
20
0
Väo
Harku
Narva
1 4 7 10 13 16 19 22 25 28 31 34 37 40 43
A
MgO
Concentration, %
25
20
15
10
5
0
Väo
Harku
Narva
1 4 7 10 13 16 19 22 25 28 31 34 37 40 43
B
CO_2
Concentration, %
50
40
30
20
10
0
Väo
Harku
Narva
1 4 7 10 13 16 19 22 25 28 31 34 37 40 43
C
Concentration, %
20
15
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0
Fe_2O_3
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Harku
Narva
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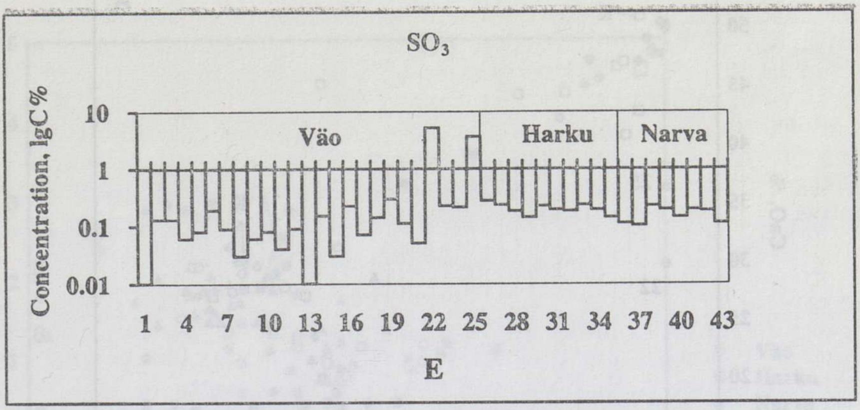


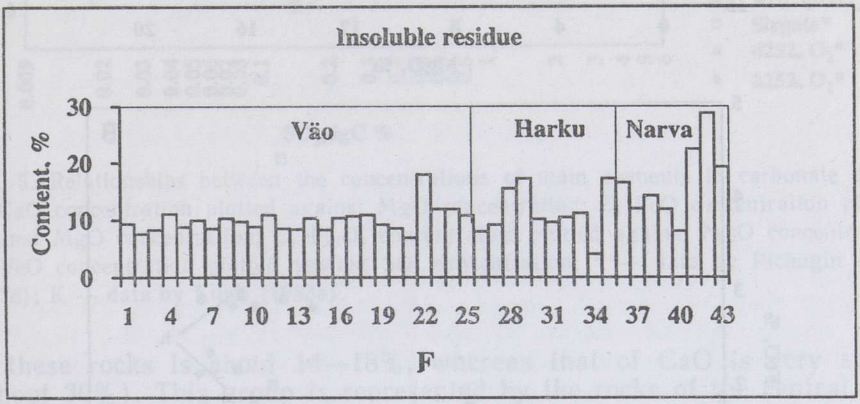
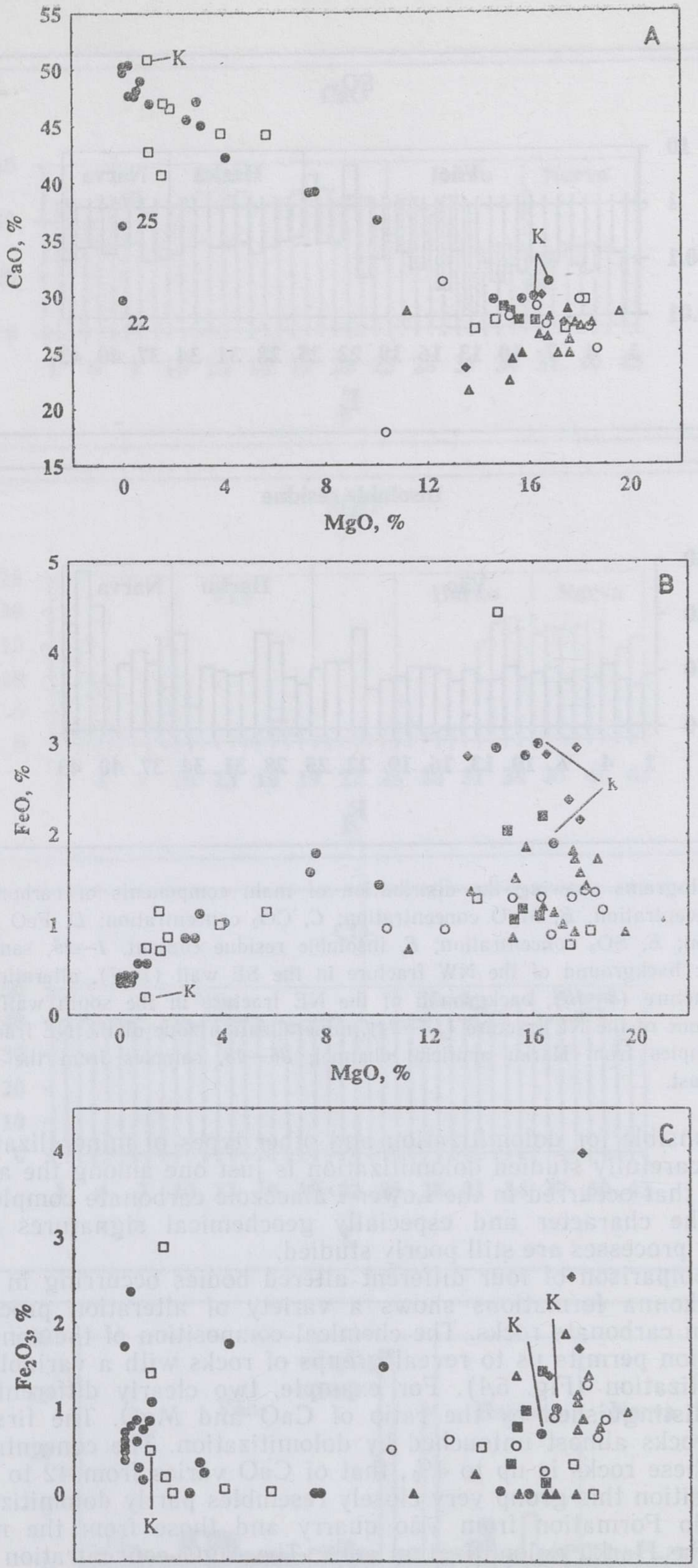


Fig. 4. Histograms showing the distribution of main components of carbonate rocks. *A*, CaO concentration; *B*, MgO concentration; *C*, CO_2 concentration; *D*, FeO and Fe_2O_3 concentration; *E*, SO_3 concentration; *F*, insoluble residue content. *1—25*, samples from Väo quarry: background of the NW fracture in the SE wall (*1—7*), alteration zone of the NW fracture (*8—13*), background of the NE fracture in the south wall (*14—16*), alteration zone of the NE fracture (*17—24*), mineralization zone of the NE fracture (*25*); *26—35*, samples from Harku artificial channel; *36—43*, samples from the Narva oil shale opencast.

was responsible for dolomitization and other types of mineralization; (3) the most carefully studied dolomitization is just one among the alteration processes that occurred in the Lower Palaeozoic carbonate complex of the region. The character and especially geochemical signatures of other secondary processes are still poorly studied.

The comparison of four different altered bodies occurring in the Väo and Viivikonna formations shows a variety of alteration processes in Ordovician carbonate rocks. The chemical composition of the zones under investigation permits us to reveal groups of rocks with a variable degree of dolomitization (Fig. 5*A*). For example, two clearly different groups may be distinguished by the ratio of CaO and MgO. The first group includes rocks almost untouched by dolomitization. The concentration of MgO in these rocks is up to 4%, that of CaO varies from 42 to 52%. In its composition this group very closely resembles partly dolomitized rocks of the Väo Formation from Väo quarry and those from the marginal parts of the Harku dolomitization zone. The MgO concentration is there usually below 10% as in other sites studied by Pichugin et al. (1978). The second group comprises the almost fully dolomitized rocks of the Viivikonna Formation of the Narva opencast. The concentration of MgO


A
CaO, %
55
50
45
40
35
30
25
20
15
K
25
22
0
4
8
12
16
20
MgO, %
B
FeO, %
5
4
3
2
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K
MgO, %
C
Fe2O3, %
4
3
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1
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K
MgO, %

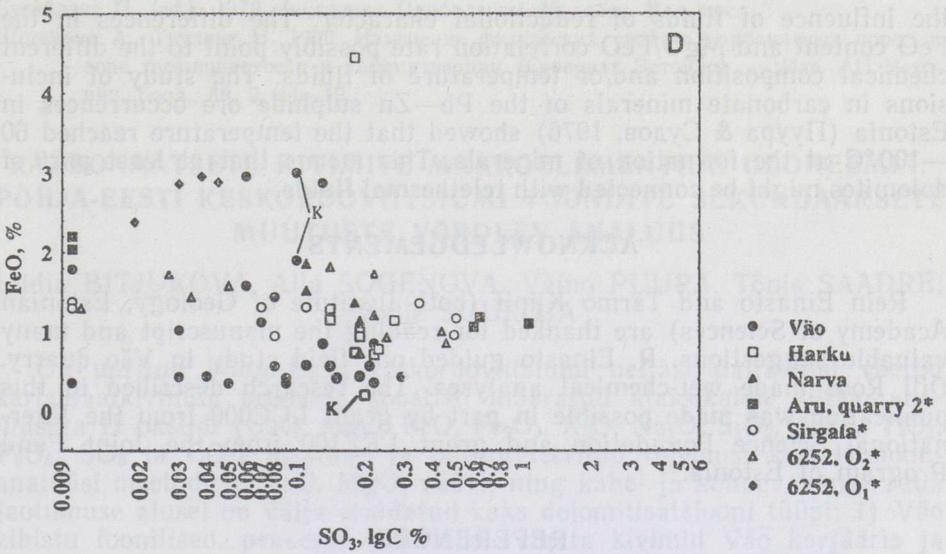

Fig. 5. Relationships between the concentrations of main elements in carbonate rocks. *A*, CaO concentration plotted against MgO concentration; *B*, FeO concentration plotted against MgO concentration; *C*, Fe_2O_3 concentration plotted against MgO concentration; *D*, FeO concentration plotted against SO_3 concentration; * — data by Pichugin et al. (1978); K — data by Kiipli (1983a).

in these rocks is about 14—18%, whereas that of CaO is very stable (about 30%). This group is represented by the rocks of the central part of the tectonic zone in Harku artificial channel and also by two samples from Väo quarry (close to the lower border of the dolomite layer of the Väo Formation). The intensity of dolomitization in the studied zones in the Narva and Harku outcrops reaches that of areal dolomitization in the dolomite layer of the Pae Member. However, more statistical material is needed to define the exact limits of the CaO and MgO concentration in the above groups and to classify the rocks more precisely. Of substantial help might be the investigation of the FeO content in dolomitized rocks increasing the number of analyses (Fig. 5*B*). At present, the dolomite bodies studied differ notably with respect to positive MgO—FeO correlation. In the Väo outcrop, for instance, the FeO concentration increases with that of MgO.

Comparative analysis of our results with the data by Pichugin et al. (1978) showed that the samples studied from Aru quarry 2 belonged to the second group. The same may be concluded for a dolomite zone in the Narva and Sirgala opencasts, although there the FeO content is lower (Fig. 5 *B*). In the samples from the Harku zone of dolomitization studied by us the concentration of FeO does not increase with the degree of dolomitization. In Estonia FeO predominantly enters the secondary dolomite as confirmed by studies of mineral dolomite (Pichugin et al., 1978), or sulphides in the case of sulphide formation. The latter is confirmed by the positive correlation between SO_3 and FeO for sulphides (samples 22, 25), although it is absent in other rocks studied. The content of Fe_2O_3 in dolomites is very stable (Fig. 5*C*) and not dependent on the MgO content. The contents of SiO_2, Al_2O_3, TiO_2, K_2O, Na_2O, occurring in the silicate minerals of the argillaceous admixture in carbonate rocks, are only slightly changing in the Väo Formation.

The results described above suggest that the dolomitization process studied in Ordovician carbonate rocks of North Estonia occurred under the influence of fluids of reductional character. The differences in the FeO content and MgO/FeO correlation rate possibly point to the different chemical composition and/or temperature of fluids. The study of inclusions in carbonate minerals of the Pb—Zn sulphide ore occurrences in Estonia (Пуура & Судов, 1976) showed that the temperature reached 60—100 °C at the formation of minerals. This means that at least part of dolomites might be connected with telethermal fluids.

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KARBONAATSETE KIVIMITE MAKROELEMENTIDE GEOKEEMIA: PÕHJA-EESTI KESKORDOVIITSIUMI VÖÖNDITE SEKUNDAARSETE MUUTUSTE VÕRDLEV ANALÜÜS

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On uuritud Põhja-Eesti keskordoviitsiumi neljast paljandist võetud karbonaatkivimite proovide koostist, määratud klassikalise silikaatanalüüsiga 12 oksiidi (CaO, MgO, FeO, Fe_2O_3, K_2O, Na_2O, SiO_2, Al_2O_3, TiO_2, P_2O_5, SO_3 ja CO_2) sisaldus ja interpreteeritud tulemusi korrelatsioonanalüüsi meetodiga. CaO, MgO, väävli ning kahe- ja kolmevalentse raua jaotumuse alusel on välja eraldatud kaks dolomitisatsiooni tüüpi: 1) Väo kihistu foonilised, peaaegu dolomitiseerumata kivimid Väo karjääris ja Harku paljandis lõhede lähedal (MgO 0—4%, CaO 42—52%); 2) Viivikonna kihistu tugevalt dolomitiseerunud kivimid Narva paljandis (MgO 14—18%, CaO ~ 30%). Väo ja Narva paljandi kivimites on kindlaks tehtud FeO ja MgO positiivne korrelatsioon. FeO kuulub peamiselt sekundaarse dolomiidi koostisse. Juhul, kui on moodustunud sulfiide, esineb FeO ja SO_3 korrelatsioon. SiO_2, Al_2O_3, TiO_2, K_2O, Na_2O esinevad peamiselt silikaatmineraalide koostises ja nende sisaldus sõltub savilisandi hulgast karbonaatkivimites. Dolomitisatsiooniprotsesside tüpiseerimine jätkub Eesti varapaleosoiliste kivimite edasisel kompleksel geokeemilisel ja petrofüüsikalisel uurimisel.

ГЕОХИМИЯ МАКРОЭЛЕМЕНТОВ КАРБОНАТНЫХ ПОРОД: СРАВНИТЕЛЬНЫЙ АНАЛИЗ ЗОН ВТОРИЧНЫХ ИЗМЕНЕНИЙ В СРЕДНЕМ ОРДОВИКЕ, СЕВЕРНАЯ ЭСТОНИЯ

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Изучен состав карбонатных пород, отобранных из четырех обнажений среднего ордовика Северной Эстонии. Определено содержание 12 окислов (CaO, MgO, FeO, Fe_2O_3, K_2O, Na_2O, SiO_2, Al_2O_3, TiO_2, P_2O_5, SO_3, CO_2) и дана интерпретация результатов с использованием корреляционного анализа. На основе распределения CaO, MgO, серы и разновалентных форм железа в породах зон вторичных изменений выделено два типа доломитизации. К первому относятся фоновые, почти не затронутые доломитизацией породы вяоской свиты карьера Вяо и породы этой же свиты вблизи трещин в обнажении Харку (0—4% MgO, 42—52% CaO). Ко второму типу принадлежат сильно доломитизированные породы вийвиконнаской свиты обнажения Нарва (14—18% MgO, ~30% CaO). В породах обнажений Вяо и Нарва установлена корреляция FeO с MgO. FeO преимущественно входит в состав вторичного доломита, а в случае образования сульфидов отмечена корреляция FeO с SO_3. Содержание SiO_2, Al_2O_3, TiO_2, K_2O, Na_2O, входящих главным образом в состав силикатных минералов, зависит от количества глинистой составляющей в карбонатных породах. Типизация процессов доломитизации будет продолжена при комплексном геохимическом и петрофизическом изучении раннепалеозойских пород Эстонии.