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# COMPOSITION OF CARBONATE ROCKS OF THE IDAVERE, JÕHVI AND KEILA REGIONAL STAGES (VIRUAN, ORDOVICIAN) IN EAST ESTONIA

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## Introduction

The composition of Estonian Paleozoic carbonate rocks has been studied for long period on the level of major components. During the official geological mapping of the territory of Estonia, taken place from 1960-s to 1980-s, a huge amount of analyses was made for many microelements from hundreds of boring cores. Most of these analyses, mainly semi-quantitative spectral analyses with abbreviated chemical analyses, were made in the laboratory of Geological Survey of Estonia in Tallinn. This material is partly analyzed statistically and published by P. Vingisaar, T. Kiipli, et al. (Vingisaar et al., 1979; 1981; Kiipli et al., 1984).

The aim of this study was to follow the distribution of major and minor elements in one sedimentary complex, limited in North Estonia by considerable discontinuity surfaces in the upper and lower boundary. This complex, including the Idavere, Jõhvi and Keila stages, is described as a distinct macrocyclite (Kõrts et al., 1991) and can be possibly subdivided into two mesocyclites. The upper mesocyclite (upper part of the Jõhvi Stage and Keila Stage) differs from lower one by clear microcyclic subdivision consisting up to 25 limestone-argillaceous limestone (or marl) cycles, traced in the whole extent of North-Estonian confacies belt (Ainsaar, 1992; 1993).

Carbonate rocks of the Idavere, Jõhvi and Keila stages formed lithostratigraphically Kahula Formation (Resheniya..., 1978), or Kahula Group (Resheniya..., 1987) by previous stratigraphic charts; later this name was used only for rocks of the Jõhvi and Keila stages (Männil, 1990). In this study the name of Kahula Group is used in its initial size to mark the whole Idavere-Keila complex in North Estonia. The complex is characterized by more or less argillaceous, wavy-bedded or semi-nodular limestone (mainly wackestone) with intercalations of marl and several thin K-bentonite layers. The thickness of the Kahula Group is 30–50 m.

## Material and methods

Many boreholes were drilled through the Ordovician in geological mapping of Jõgeva District (East Estonia) of scale 1 : 50 000 by Geological Survey of Estonia in late 1980-s. For this study 93 samples were collected from 28 m of section of boring core Tähkvere-704 and 4 additional samples from the Keila Stage of boring core Vaali-707 (Fig. 1).

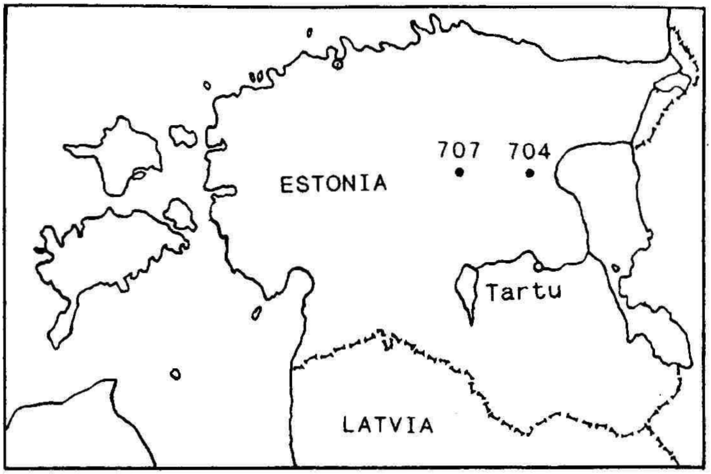


Fig. 1. Location of boreholes Tähkvere-704 and Vaali-707.

The samples were analyzed for 42 chemical elements and for insoluble residue in the laboratory of Geological Survey of Estonia in Tallinn in 1990. Main components of rock (CaO, MgO and insoluble residue) were determined by abbreviated chemical analysis. For Pb, Sr, Rb, Y and Zr the samples were analyzed by X-ray fluorescence spectroscopy and for Si, Al, Fe, Na, Ti, B, Ba, Ga, Sc, V, Cr, Mn, Co, Ni, Cu and Yb by spectral analysis. Determinations of 18 elements contained in many samples concentrations below the limit of detection and were ignored in this study. Content of $CO_2$ was also excluded because it is occurring only in compounds with Ca and Mg in the limestones. The methodology, limits of detection and variations of results for spectral analysis in the laboratory of Tallinn are described by Vingisaar et al. (1981) and Kiipli et al. (1984).

The chemical data was subjected to statistical analyses. Basic statistics such as mean and variance were calculated for each element in lithologically different parts of the complex and correlation analyses were performed on the whole group. Factor analysis was used to group the elements to associations.

## Statistical results

Correlation graph of linear pairways correlation coefficients and factor analysis showed the occurrence of following associations of chemical elements in the limestone and marl of the Kahula Group in East Estonia (samples of K-bentonites were excluded):

I. Terrigenous association: Rb, Zr, Ga, Cr, V, Ti, Si, B, Co, Y, Ba, Na, Sc, Fe, Yb, Ni, Cu and Al (in the order of correlation coefficient with content of insoluble residue);

I.a. Clay association: Al, Si, Ba, Rb, Cr, Ga, Yb, Zr, Ti and Sc (in the order of coefficients with Al);

I.b. Iron association (pyrite): Fe, Co, V and Ni;

II. Dolomite association: Mg, Mn, (Fe);

III. Calcite: Ca;

IV. Sr;

V. Pb.

These results are generally similar to data of the whole Ordovician and Silurian carbonate complex of Estonia (Vingisaar et al., 1981; Kiipli et al., 1984) and show that the distribution of majority of studied elements depends on content of argillaceous material in the rocks. The only notable difference is clear relation of yttrium, considered by Kiipli et al. (1984) to be related with phosphates, with terrigenous association, which may be explained by very small concentration of phosphorus ($<0.06\%$ of P) in the studied rocks.

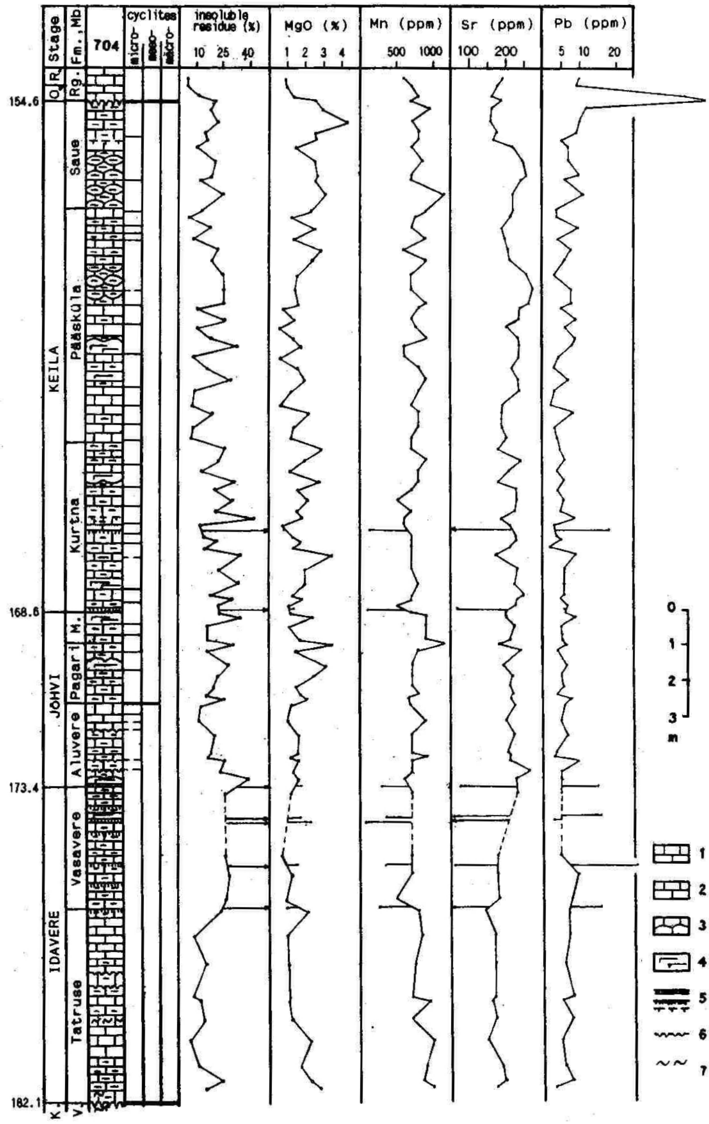


**Fig. 2.** Distribution of insoluble residue and elements in the boring core Tähkvere-704. Values corresponding to the K-bentonites are shown out of the curve;

1 – limestone; 2 – argillaceous limestone; 3 – semi-nodular structure; 4 – marl; 5 – K-bentonites; 6 – discontinuity surface; 7 – kukersite. Regional stages: K. – Kukruse; O. – Oandu; R. – Rakvere. Formations and members (Fm., Mb.): V. – Viivikonna; M. – Madise; Rg. –Rägavere.

**Table 1.** Mean and standard deviation of insoluble residue (i.r.) and elemental concentrations in boring cores 704 and 707 by traditional lithostratigraphic units, in the whole Kahula Group (carbonate rocks only) and in K-bentonites (in ppm unless otherwise noted; number of samples in parentheses; methods: oxides – by chemical analysis, * – by X-ray fluorescence spectroscopy, all others – by spectral analysis)..

| | Tatruse | Vasavere | Aluvere | Pagari, Madise & Kurtna | Pääsküla | Saue | Kahula Group | K-bentonites |
|---|---|---|---|---|---|---|---|---|
| | (10) | (4) | (8) | (30) | (23) | (12) | (87) | (7) |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| i.r. (%) | 13.9±5.9 | 27.0±1.3 | 20.5±8.9 | 22.7±7.7 | 16.2±8.3 | 17.7±4.1 | 19.3±7.9 | 85.9±3.0 |
| CaO (%) | 44.4±4.1 | 38.1±1.0 | 41.4±5.9 | 38.8±5.7 | 43.7±5.8 | 39.6±4.4 | 41.1±5.6 | 1.9±1.1 |
| MgO(%) | 1.6±0.7 | 1.0±0.3 | 1.4±0.3 | 1.8±0.7 | 1.5±0.6 | 3.7±2.4 | 1.9±1.3 | 1.2±0.4 |
| Si (%) | 10±5 | 20±8 | 14±5 | 16±6 | 11±7 | 11±4 | 13±6 | |
| Al (%) | 2.9±1.6 | 2.6±0.5 | 3.3±1.4 | 3.8±1.5 | 2.5±1.6 | 3.2±1.5 | 3.2±1.5 | 15.1±2.0 |
| Fe (%) | 1.2±0.4 | 1.0±0.4 | 1.4±1.1 | 1.7±0.9 | 1.1±0.7 | 1.5±0.8 | 1.4±0.8 | 5.4±2.0 |
| Na (%) | 0.10±0.02 | 0.12±0.02 | 0.10±0.03 | 0.12±0.03 | 0.11±0.03 | 0.10±0.02 | 0.11±0.03 | 0.16±0.01 |
| Ti (%) | 0.15±0.04 | 0.17±0.04 | 0.16±0.03 | 0.17±0.04 | 0.15±0.04 | 0.15±0.03 | 0.16±0.04 | 0.32±0.11 |
| Pb* | 6± 2 | 7±2 | 6±2 | 6±2 | 6±2 | 12±11 | 7±5 | 14±8 |
| Sr* | 166±16 | 190±27 | 220±20 | 214±22 | 220±25 | 186 ±52 | 206±33 | 58±11 |
| Rb* | 20±11 | 28±8 | 29±12 | 39±18 | 26±18 | 27±7 | 30±17 | 98±12 |
| Y* | 17±2 | 18±3 | 17±4 | 18±3 | 14±4 | 13±3 | 16±4 | 36±10 |
| Zr* | 66±18 | 72±15 | 72±20 | 76±17 | 67±19 | 68±11 | 71±18 | 273±88 |
| B* | 32±11 | 70±20 | 44±20 | 48±23 | 37±28 | 23±6 | 40±24 | 125±14 |

Table 1 (järg)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| Ba | <110±40 | 130±30 | 170±50 | 170±40 | <110±50 | 140±30 | <140±50 | 350±50 |
| Ga | <4±1 | 7±2 | <5±2 | 6±2 | <5±2 | <5±1 | <5±2 | 21±4 |
| Sc | <4±3 | 4±1 | <5±3 | <6±3 | <3±3 | 5±2 | <5±3 | 14±4 |
| V | 15±4 | 22±4 | 18±7 | 24±9 | 19±7 | 21±5 | 21±7 | 78±32 |
| Cr | 26±8 | 39±11 | 27±10 | 34±12 | <21±10 | <21±6 | <27±12 | 42±29 |
| Mn | 850±110 | 650±100 | 740±110 | 730±130 | 770±100 | 840±150 | 770±130 | 220±120 |
| Co | <4±1 | 5±1 | <4±2 | 6±2 | <4±1 | <4±1 | <4±2 | 10±4 |
| Ni | 13±3 | 13±2 | 14±5 | 13±3 | 12±4 | 12±3 | 13±3 | 29±8 |
| Cu | 7±1 | 9±2 | 9±2 | 10±3 | 9±3 | 8±1 | 9±3 | 16±5 |
| Yb | <2±1 | 3±0 | 2±1 | 3±1 | <2±1 | <2±1 | <2±1 | 4±1 |
| K (%) | | | | | | | | 7±2 |
| Th* | | | | | | | | 14±3 |
| Nb* | | | | | | | | 17±6 |
| Zn | | | | | | | | 25±10 |
| Be | | | | | | | | 4±2 |
| La | | | | | | | | 24±10 |

The content of magnesium is slightly related with iron and terrigenous association, which is common for Estonian carbonates and can be explained by similar behaviour of many metals in sorption from seawater to clay particles and in later diagenetic transformation to dolomite (Mg), sulphides or moving to the structure of clay minerals (Kiipli et al., 1984).

Strontium has clear negative correlation with magnesium (correlation coefficient $r = -0.50$) and was obviously partly removed by dolomitization (Taalmann et al., 1977). Strontium has some positive correlation with several elements of terrigenous association (Ba, B, Cu, Si, Ti) but not with calcium ($r = 0.04$). Lead is slightly correlated with iron association (Fe, V), occurring probably with them in some sulphide-rich rocks like pyritized limestone below discontinuity surfaces.

## Distribution of elements in the sequence

The mean values and standard deviations of elemental concentrations and of insoluble residue content in traditional lithostratigraphic units and in limestone and marl of the whole Kahula Group are shown in the Table. Lithologically very similar Pagari, Madise (in the Jõhvi Stage) and Kurtna "members" (in the Keila Stage) are taken together. Vasavere and Pagari-Madise-Kurtna beds represent more argillaceous parts of the lower and upper mesocyclite, respectively; Tatruse and Pääsküla beds are less argillaceous parts of them. The uppermost part, Saue "member", is argillaceous limestone differing from the rest of the complex by presence of some shell accumulations. Vertical distribution of insoluble residue and of selected elements in the Tähkvere-704 boring core is shown in Fig. 2.

Distribution of most of the elements is determined by content of argillaceous material. The variance of this component is controlled mainly by microcycles, particularly in the upper mesocyclite. Meso- and macrocyclites have also some influence to distribution of argillaceous material, as it is seen in the Table by means of insoluble residue content, but this variance is not so wide as in microcyclites. Content of argillaceous material and of most of the elements of this group varies 3–5 times in microcyclites whereas mean values for the parts of the meso- and macrocyclites vary only 1.2–2 times. For this reason, the distribution of majority of elements in the sequence is determined by microcyclicity.

Considering the magnesium to be related mainly with dolomite, the calculated content of this mineral in the main part of the studied interval of Tähkvere-704 core is 3–15% (mean ~8%). The uppermost 1–1.2 m of Keila Stage below the significant discontinuity surface is containing dolomite 13–18% in boring core 704 and uppermost 1.4 m in boring core Vaali-707 even 40–42% (by two samples; the third sample 4 m below the discontinuity surface contained 6% of dolomite). Content of strontium in this layer is 1.5–2 times lower than average. Low values of strontium content are common for secondary dolomitized limestones (Taalmann e.a., 1977; Kiipli, 1983; Tucker, Wright, 1990). The higher dolomitization of only about meter-thick bed below the discontinuity surface, marking considerable sedimentary gap in Middle Ordovician, may refer to possible early dolomitization of limestones started already during the existence of hardground environment. This process might take place in a mixing zone of fresh groundwater (or meteoric water) and percolating seawater (Kiipli, 1983; Moore, 1989). T. Kiipli (1983) refers to examples, if upper 1–3 metres of the Pirgu and Jaagarahu stages are dolomitized below the overlying regressive beds.

The more realistic explanation for magnesium and strontium distribution pattern in the sequence (particularly in the Vaali-707 core) is secondary post-Ordovician selective dolomitization. In many boring cores of East Estonia the aphanitic pure limestone of Rägavere Formation (Voore Group), overlying the Idavere-Keila argillaceous complex, is strongly affected by post-Ordovician dolomitization. This process was usually stopped in the rapid lithological boundary between the Kahula and Voore groups (Keila and Oandu stages) and underlying argillaceous limestone remained undolomitized. However, the limit of secondary changes of limestone was not so rapid and uppermost part of the Keila Stage is often more or less dolomitized (data by Ain Põldvere). That was partly caused by absence of marl layer of the Hirmuse Formation (Oandu Stage) in this boundary in central part of East Estonia. After T. Kiipli (1983) large dolomitization of Ordovician and Silurian limestones took place under the bottom of Devonian sea in an intermixture zone of groundwater and seawater.

Very high concentration of lead (5–6 times higher than average) is related with the same discontinuity surface in the upper boundary of the Keila Stage (and of the macrocyclite). This surface is characterized by pyritized impregnation zone with thickness 15–25 cm below the surface and by long vertical and subhorizontal pyritized borings, reaching up to 15 cm from the surface. The impregnation zone is dark in colour because of fine pyrite crystals, but 20 cm of light-coloured aphanitic limestone of Oandu Stage above the surface contains big pyrite crystals of 0.5–1 cm in size. Both rocks sampled 5 cm above and below the surface have very high lead content. The abundance of pyrite with high lead content in overlying bed may be caused by replacement of sulphides from discontinuity surface impregnation zone to surrounding limestones after early diagenesis. There are described examples in the world, if formation of ore of Pb-Zn-Fe sulphides is related with discontinuity (emersion) surfaces and unconformities in the carbonate rocks (Flügel, 1982).

It must be taken into account that rapid lithological boundary between the Kahula and Voore groups might work as geochemical barrier, causing some sulphide mineralization and stratigraphically traced dolomitization in East Estonia.

## K-bentonites

There are at least 17 thin (up to 10 cm) layers of K-bentonite or bentonitic marl in the Idavere, Jõhvi and Keila stages in East Estonia, 6 of which in the Tähkvere-704 core were sampled and analyzed (Table). These results are quite similar to composition of North American K-bentonites of the same age, analyzed by Kolata et al. (1986). East Estonian bentonites seem to be more rich in Na, Fe, Cr, Yb and La and more pure in Zn content than North American ones, although, the laboratory methods used are not comparable.

## Conclusions

The majority of elements in the Kahula Group are related with terrigenous material and therefore their distribution in the sequence is controlled mainly by microcyclical variation of argillaceous material. Macro- and mesocyclites in the Idavere-Keila complex control only slightly these variations. The most notable variations in magnesium, strontium and lead concentrations in the sequence are related with secondary changes of carbonate rocks nearby discontinuity surface and significant lithological boundary between the Kahula and Voore groups.


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## IDAVERE, JÕHVI JA KEILA LADEME KARBONAATKIVIMITE KOOSTIS IDA-EESTIS

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### Resümee

Uuriti 23 keemilise elemendi ja lahustumatu jäägi jaotust ühte makrotsükliiti esindavas Kahula ülemkihistus kahes Ida-Eesti läbilõikes. Geokeemiliste (röntgenfluoressents, spektraal- ja lühendatud keemilise analüüsi) andmete statistilise töötluse tulemusel eraldati terrigeense komponendiga seotud ja sellest sõltumatud (Mg, Mn, Sr, Pb) elemendid ning leiti iga elemendi põhilised statistilised näitajad erinevate litoloogiliste ühikute kaupa. Terrigeense komponendiga seotud elementide sisaldust kontrollib põhiliselt sedimentatsiooniline mikrotsüklilisus, sisalduste varieeruvus makro- ja mesotsüklii-tide erinevate osade vahel on tunduvalt väiksem. Suurimad kõikumised magneesiumi, strontsiumi ja plii sisaldustes on seotud sekundaarsete protsessidega lubjakivis Keila ja Oandu lademe piiril, mis kujutab püriitset katkestuspinda koos suure litoloogilise muutusega.