

VILNIUS UNIVERSITY
NATURE RESEARCH CENTRE

Eugenija RUDNICKAITĖ

**CARBONATES IN THE LITHUANIAN QUATERNARY SEDIMENTS AS
LITHOSTRATIGRAPHIC CRITERION AND INDICATOR OF
PALAEOCLIMATIC CONDITIONS**

Summary of Doctoral Dissertation

Physical Sciences, Geology (05P)

Vilnius, 2016

The dissertation was carried out at the Vilnius University in 2012-2016

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The official defence of the doctoral dissertation will be held at the public meeting of the Council of Scientific Field of Geology on December 28, 2016, at 13:00 in the “Great auditorium” (214) of the Faculty of Natural Sciences of Vilnius University.

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The summary of the dissertation was distributed on November 28, 2016.

The dissertation is available at the libraries of Vilnius University and the Nature Research Centre and at the VU website: www.vu.lt/naujienos/ivykiu-kalendorius.

VILNIAUS UNIVERSITETAS
GAMTOS TYRIMŲ CENTRAS

Eugenija RUDNICKAITĖ

**LIETUVOS KVARTERO NUOGULŲ KARBONATINGUMAS KAIP
LITOSTRATIGRAFINIS KRITERIJUS IR PALEOKLIMATINIŲ
SĄLYGŲ INDIKATORIUS**

Daktaro disertacijos santrauka

Fiziniai mokslai, Geologija (05P)

Vilnius, 2016

Disertacija rengta 2012–2016 metais Vilniaus universitete.

Mokslinis vadovas:

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Disertacija bus ginama viešame Geologijos mokslų krypties tarybos posėdyje 2016 m. gruodžio mėnesio 28 d., 13:00 val. Vilniaus universiteto Gamtos mokslų fakulteto Didžiojoje auditorijoje (214).

Adresas: M. K. Čiurlionio g. 21/27, LT-03101, Vilnius, Lietuva.

Disertacijos santrauka išsiųsta 2016 metų lapkričio 28 d.

Disertaciją galima peržiūrėti Vilniaus universiteto, Gamtos tyrimų centro bibliotekose ir VU interneto svetainėje adresu: www.vu.lt/naujienos/ivykiu-kalendorius.

ABBREVIATIONS:

d:c – ratio of dolomite versus calcite

DIC – Dissolved inorganic carbon

ESR – Electron spin resonance (electron paramagnetic resonance)

INQUA – The International Union for Quaternary Research

MIS – Marine Isotope Stages

YDB – Younger Dryas Boundary

OCB – Ocean Carbon Biogeochemistry

P – Van der Waerden criterion. In previous works also referred to as X or P

SAS – Statistical Analysis System

SEM – Scanning electron microscope

SEM-BSE – Backscattered electron images

SEM EDS – Energy dispersion spectrum

SEM SE – Secondary electron images

LGS – Lithuanian Geological Survey

RCL – Research Council of Lithuania

LSSF – The Lithuanian State Science and Studies Foundation

INTRODUCTION

The present dissertation is a generalization of the research material collected and analysed by the author individually or through participation in collective research projects in 1980–2015. The greater part of the research was conducted during the geological doctoral studies at the Vilnius University (2012–2016) and through participation in the implementation of the budgetary research themes at the Department of Geology and Mineralogy of Vilnius University and in the research teams for projects sponsored by the Research Council of Lithuania (RCL). The research material was collected by studying the boreholes and outcrops in the territory of Lithuania.

Theoretical assumptions and relevance of the present study

The stratigraphic subdivision and correlation of Quaternary deposits is a procedure, which allows revealing the geological composition of Quaternary thickness, understanding its formation patterns, reconstructing palaeogeographical conditions at different periods, etc. All these aspects are important for Lithuanian researchers and researchers from other regions with similar geological Quaternary structure. The main biostratigraphic principle used in geology is insufficient for stratigraphic subdivision of the Quaternary due to a very simple reason: the greater part of the Quaternary thickness – i.e. the Pleistocene deposits – are paleontologically “mute”. Due to specific character, the geochronological research methods not always facilitate solutions of the issues related with stratigraphic correlation. Some of them allow dating only the young deposits and sediments (e.g. radiocarbon method) whereas the possibilities of other methods are limited by the spectrum of the genetic types of deposits and sediments suitable for dating, (e.g. glacial deposits are unsuitable for luminescence dating). Various lithological criteria are commonly used for correlation of the “mute” Pleistocene deposits. The till layers are the best preserved and the most solid indicators of former glaciations, thus usually serve as the basis for correlation of the “mute” deposits. Yet the reliability of stratigraphic correlation of tills particularly depends on the chosen lithostratigraphic criteria and possibilities of application. Therefore, the search for new lithostratigraphic

criteria remains a relevant issue of Quaternary geology in all regions affected by continental glaciation.

The Lithuanian Pleistocene tills are rich in carbonaceous material. Therefore, investigation of carbonate minerals as potential lithostratigraphic criteria and indicators of palaeogeographical conditions was chosen as the main objective of the present dissertation. The dissertation is comprised of two sections: the main section is devoted to investigations of carbonate quantities in the Pleistocene tills and finding out the effective lithostratigraphic criteria; the second represents an analysis of specific formation patterns of carbonates and their relationship with interglacial climate changes. In the light of available information about the Quaternary structure of Lithuania and adjacent regions, lithological peculiarities of the sub-Quaternary substratum (pre-Quaternary rocks), dynamic character of Pleistocene continental glaciers, changes of palaeogeographical conditions, etc., two main hypotheses were suggested: 1) carbonate content in the till deposits and the ratio between the content of some carbonate minerals presumptively reflect the directions of glaciers advances therefore could serve as a basis for stratification of “mute” deposits; 2) composition, content and content variation pattern of carbonates presumably reflect the climatic conditions during non-glacial sedimentation therefore could facilitate partial reconstruction of palaeogeographical sedimentary environment.

Based on these hypotheses, the objective and goals of the dissertation were formulated.

Objective and goals

The objective of the present study was to evaluate the possibilities to use the research data about carbonates in tills for stratigraphic classification and correlation of the Pleistocene deposits in the territory of Lithuania and for reconstruction of interglacial and post-glacial palaeogeographical conditions.

The main goals are as follows:

- 1) to investigate carbonate content in heterochronous till deposits and statistically analyse the obtained data;

- 2) to evaluate the possibility to use the carbonate content research data for stratigraphic correlation of investigated deposits and to identify the optimal lithostratigraphic criteria;
- 3) based on the obtained results about carbonate content, to develop methodology of stratigraphic correlation of tills using mathematical statistical methods;
- 4) to investigate carbonate content in heterochronous non-glacial deposits for determining the correlation of carbonate content with sedimentation environment and climate changes.

Scientific novelty

The author conducted the investigation of carbonate content in the Quaternary glacial and non-glacial deposits – the bulk content of carbonates and the content of carbonate minerals calcite and dolomite each – individually – for the first time in Lithuania.

The author original suggestion is that the content ratio dolomite versus calcite should be used instead of the absolute content values of carbonate minerals dolomite and calcite as a lithostratigraphic criterion for classification of glacial deposits. An original methodology for stratigraphic correlation of tills using mathematical statistical methods (Van der Waerden criterion) was developed.

For the first time in Lithuania, the content of carbonate minerals dolomite and calcite and the bulk content of carbonates were compared with the results of pollen and diatomic analysis.

Theoretical and practical significance

The present study complements the theoretical knowledge about the texture and structure of glacial and non-glacial deposits and climate oscillations during their formation.

Of practical significance is the distinguished lithostratigraphic criterion (dolomite versus calcite ratio) which served as a basis for development of methodology for identification of heterochronous tills. The developed methodology is applicable in

geological scientific research and practical works – in geological mapping of Quaternary deposits.

Maintained propositions

The achieved goals and obtained results allowed formulating the following maintained propositions:

1. The minerals of carbonate class – dolomite and calcite – in the Lithuanian Pleistocene glacial deposits are allochthonous, i.e. dislocated and accumulated by glaciers.
2. The bulk carbonate content in the Pleistocene glacial deposits and the ratio of carbonate minerals dolomite versus calcite reflect the directions of glaciers advance and may serve as a basis for lithostratigraphic subdivision and correlation of the “mute” layers of deposits (Pleistocene tills);
3. The composition, content and content variation patterns of carbonate minerals in non-glacial sediments reflect the climate conditions during sedimentation and allow reconstructing the general features of palaeogeographical conditions.

Presentation of results

The main results of the study were presented, discussed and debated at the following scientific conferences:

1. XI INQUA congress. Russia, Moscow, 1982 08 01–09.
2. International Conference and field symposium „Decoding the Last Interglacial in Western Mediterranean“, Sardinia, Italy, 2010 10 25–29.
3. XVIII INQUA congress: „Quaternary sciences – the view from the mountains“. Switzerland, Bern, 2011 07 21-27. [2 presentations]
4. International Conference and field symposium “Late Glacial Maximum in the Valday Region, NW Russia”. INQUA Peribaltic Working Group, Russia, 2012 09 13–17. [2 presentations]

5. „Jūros ir krantų tyrimai – 2013: 7-oji nacionalinė jūros mokslų ir technologijų konferencija“. (Marine and coastal research – 2013: the 7th national conference of science and technologies) Klaipėda, 2013 04 3–5.
6. International Conference and field symposium „Palaeolandscapes from Saalian to Weichselian, South Eastern Lithuania“. INQUA Peribaltic Working Group, Lithuania, 2013 06 25-30. [2 presentations]
7. VU Gamtos mokslų fakulteto Geologijos ir mineralogijos katedros metinė doktorantų konferencija „Nuo Žemės mantijos iki kvartero Lietuvoje“. (Annual conference of doctoral students „From the Earth’s Mantle to the Quaternary in Lithuania“ organized by the Department of Geology and Mineralogy of the Faculty of Natural Sciences, Vilnius University). Vilnius, 2013 11 28.
8. International Conference and field symposium „Late Quaternary terrestrial processes, sediments and history: from glacial to postglacial environments, Eastern and Central Latvia“. INQUA Peribaltic Working Group, Latvia, 2014 08 17– 22.
9. The 9th Baltic Stratigraphical Conference, Lithuania, 2014 09 8–9.
10. VU Gamtos mokslų fakulteto Aštuntoji mokslinė konferencija „Mokslas Gamtos mokslų fakultete“. (The 8th scientific conference „Science at the Faculty of Natural Sciences“ at the Faculty of Natural Sciences, Vilnius University). Vilnius, 2014 10 03.
11. Annual conference of doctoral students of geology „From Silurian to Quaternary in Lithuania“. Vilnius University, Department of Geology and Mineralogy of the Faculty of Natural Sciences. Vilnius 2014 11 27.
12. XIX INQUA Congress: „Quaternary Perspectives on Climate Change, Natural Hazards and Civilization“. Japan, Nagoya, 2015 07 26 – 08 02. [2 presentations]
13. Annual conference of doctoral students of geology. Vilnius University, Department of Geology and Mineralogy of the Faculty of Natural Sciences, Vilnius, 2015 11 19.
14. International conference „From Star and Planet Formation to Early Life“. Vilnius, 2016 04 25–28.
15. International Conference and field symposium „Quaternary geology of north-central Poland: from the Baltic Coast glacial to the LGM limit“. INQUA Peribaltic Working Group, Poland, 2016 08 28–09 02.

Publications

The research results obtained during the doctoral studies were published in scientific journals and other editions: 4 publications in ISI Web of Science journals, 3 in ISI Master List journals, 1 in other peer-reviewed journals, 1 in international conference materials, 1 in other editions. The list of publications is given in section “List of Publications and Scientific Projects by the Author.”

Extent and structure

The doctoral dissertation is composed of an Introduction, three main chapters, Conclusions, List of References, and List of Author’s Publications and Scientific Projects. The dissertation is comprised of 151 pages including 65 illustrations and 17 tables. The List of References has 136 entries.

Acknowledgement

My cordial thanks go to scientific supervisor Prof. Dr. Albertas Bitinas for every kind of support.

I am grateful to Doc. Dr. Antanas Brazauskas and Doc. Dr. Rūta Levulienė for useful consultations in choosing and applying statistical methods, Dr. Žydrūnas Dėnas for technical aid, Dr. Rimantė Guobytė for constructive criticism, colleague Monika Melešytė for shearing information and aid in field works, colleague Julius Vainorius for new research objects and aid in field works.

I appreciate the staff of the Department of Geology and Mineralogy for creating the atmosphere favourable for scientific research work.

I remember with gratitude my first scientific supervisor deceased Doc. Dr. Petras Vatiekūnas who taught me to evaluate critically, generalize and present the obtained results.

I am also grateful to deceased Hab. Dr. Prof. Algirdas Juozapas Gaigalas for his efforts to retain me in the field of scientific research.

I give my thanks to the Dean of the Faculty of Natural Sciences Prof. Dr. Osvaldas Rukšėnas for encouragement to enter doctoral studies.

The Lithuanian Research Council allotted additional grant for scientific research and academic trips during doctoral studies.

My special thanks go to my Husband, Son and Daughter for encouragement, support and understanding.

1. OVERVIEW OF RESEARCH

The extensive distribution of carbonaceous rocks, diversity of formation patterns and their changes during the evolution of the Earth are aspects of paramount scientific importance because the knowledge of the composition of carbonaceous rocks is informative about the palaeoenvironmental conditions (Trimonis, 2005). Though the “classical” carbonaceous rocks are absent in the our investigated sedimentary environments (glacial regions; lakes and bogs; partly rivers) and we only can speak about carbonate content in sediments, the scientific importance of research is not insignificant. The carbonate constituent of these formations also reflects the past environmental conditions.

The content of carbonates in glacial material deposited in the sedimentary environment of continental glacial regions largely depends on the lithological composition of rock substratum exarated by advancing glaciers (Flint, 1957; Рухина, 1960; Dreimanis, 1961; Паукас, 1961; Dreimanis & Vagners, 1965; 1969; Vagners, 1966; Рухина, 1973; 1974; Горецкий, 1973; Лаврушин, 1976; Лукашев, 1970; Лукашев, Астапова, 1971, and others). A. Dreimanis and G. H. Reavely, who investigated tills of Canada in 1953 (Dreimanis & Reavely, 1953) were pioneers of carbonate content investigations. They discovered the bimodal distribution of carbonates in granulometric fractions of tills. A. Dreimanis used calcimeter for quantitative evaluation of calcite and dolomite in tills (Dreimanis, 1962). In 1971, having gained long-term experience, A. Dreimanis with co-author U.J. Vagners published a comprehensive generalizing article about the distribution patterns of carbonates in tills. The distribution patterns of carbonates and the bimodal distribution of various minerals in tills also were analysed by researchers from the neighbouring counties A. Raukas

(1961) from Estonia, A. Savaitovas (Савваитов, 1962; 1962a) and A. Stinkule (Стинкуле, 1964) from Latvia.

A.V. Matvejev (Матвеев, 1976) pointed out that the bulk carbonate content and the composition of carbonate minerals can be taken as correlation marker of till layers in Belarus. The differences of carbonate content in heterochronous till layers were determined by Estonian scientist A. Raukas (Раукас, 1978).

I.J. Fairchild & B. Spiro (1990) reported that carbonate minerals in glacial deposits could serve as geochemical indicators of palaeoenvironment.

The mentioned and many other research works allow assuming that the composition and ratio of carbonate minerals also could be taken as correlation marker in other territories of continental glaciation.

In the 21st century, some researchers view carbonate content in non-glacial sediments as an indicator of climate oscillations along with palynological, diatomic and palaeocarpological indicators (Leng, & Marshall, 2004; Michczyński et al., 2013; Stankevica et al., 2015; Zernitskaya et al., 2015; Rae et al., 2014, and others). Yet it should be mentioned that only calcite is determined and, almost exclusively, by incineration.

In Lithuania, generalizing studies devoted to carbonate content investigations in the Quaternary tills alone are lacking. Meanwhile, the carbonate component represents a significant part of Pleistocene tills. The content of carbonates in tills depends on such factors as: assimilation of carbonaceous rocks by advancing glacier bed, appearance of new carbonate minerals in till strata during the stages of transition and early genesis of glacial debris, formation of carbonate minerals under hypergenetic conditions, etc. Carbonate content in tills is closely related with the glacial relief and composition of rocks. Carbonaceousness of the deposits left by glacier advance over carbonaceous rocks is higher. It is also higher in the areas where carbonaceous rocks formed relief elevation in the path of advancing glacier. The composition of carbonate minerals mainly depends on the lithological composition of glacial bedrock. The distribution of carbonate minerals in the granulometric spectrum is uneven. Two modes can be observed in the distribution curve (Гайгалас, 1964). One mode ranges within the limits of coarse fractions (30–3 mm). It is composed of the fragments of limestone, dolomite, chalk and other carbonate rocks. The other mode ranges within the interval of fine (aleurite; 0.1–

0.01 mm) fractions and is correlated with the increase of the content of carbonate minerals (calcite, dolomite, etc.). The bimodal distribution of carbonates in the granulometric spectrum is a fingerprint of splitting and attrition processes taking place in the ice sheet during transportation of material eroded away from the sedimentary rock substratum. The data about carbonate distribution illustrate disintegration of rock debris into constituent parts – minerals.

A. Klimašauskas pointed out the uneven distribution of various minerals in the granulometric spectrum of tills (Климашаускас, 1965). He also considered the possibility to apply the distribution of minerals for stratigraphic subdivision of the Quaternary deposits (Климашаускас, 1967). A. Bitinas, A. Bitinas and R. Zinkutė (Битинас, 1991; Битинас & Зинкуте, 1993; and others) investigated the problems related with employment of statistical methods (using computers) for stratigraphic correlation of tills.

A. Gaigalas (1979) maintained that coarse clastic material of some Lithuanian tills contain elevated quantities of dolomite fragments. Also it was determined that calcite and dolomite are dominant carbonate minerals in the Lithuanian glacial deposits; the content of other carbonate minerals is negligible (Рудницкайте, 1980). Attempts were made to apply carbonaceousness, as one of the indicators, to stratigraphic subdivision of tills using statistical methods (Гайгалас и др., 1985). Yet at the time, researchers confined to application of Student's criterion and D. A. Rodionov's (Родионов, 1968) method.

Glacial deposits (tills) without palynologically identifiable interglacial sediments are stratigraphically “mute” and their precise (or absolute) dating is possible in very rare cases. For this reason, collation and stratigraphic subdivision of glacial deposits require their complex analysis. Following this path, V. Baltrūnas (1995) divided the stratigraphic subdivision and collation methods (for investigation of Pleistocene deposits) into four groups: investigation methods of structure and composition, investigation methods of physical properties, and methods of absolute dating.

The structural-facies or structural palaeogeomorphological method has been used for understanding the structure of the Quaternary thickness, for geological mapping in particular, since long ago. Using this method, the Quaternary deposits is analysed drawing the intersecting geological sections and compiling maps displaying the

distribution, thickness, and isolines of the altitudes of the bed and roof of deposits. Analysis is based on the macroscopic features of deposits (including tills): colour, hardness, and specific features of structure and texture. The measurements of long-axis orientation and angle of gravel and pebbles are informative about glacial deposits. Also important are investigations of their physical properties: geophysical parameters and residual magnetism (Baltrūnas, 1995).

Only a few methods are employed for determining the absolute age of tills. One of them is cosmogenic (^{10}Be) dating of big (1.5–2 m in height) natural boulders. This method is used to determine the time of glacier melting when the surface of the boulder became exposed to cosmic radiation. In this way, the age of the till containing the boulder is discovered. In Lithuania, almost 30 natural boulders were dated using this method revealing the time of deglaciation of the terrains (Rinterknecht ir kt., 2008). This method is very expensive and applied for dating of exposed deposits alone. Meanwhile, investigations of Lithuanian tills are confined to dating their relative age. The commonly applied methods for this purpose are: investigation of granular, mineral and chemical composition of glacial deposits, investigation of petrographic composition of coarse fraction (coarse gravel–fine pebbles), and identification of endemic boulders. The long-term data accumulated by Lithuanian researchers by the mentioned methods displayed the differences in granular, chemical and mineral composition of heterochronous tills (Baltrūnas, 1995; Guobytė, Satkūnas, 2011). The method of determining the petrographic composition of gravel–pebbles contained in the tills, elaborated by A. Gaigalas and M. Melešytė, allows stratigraphic subdivision of glacial deposits according to the available results (Gaigalas, 1979). This method is very supportive in analysing till horizons in outcrops. Yet when only a sample core is available, the method is not always applicable because due to the limited core mass the minimal necessary amount of pebbles cannot be collected.

The rarely used analytical investigation of carbonate amount in deposits, presented in this study, could be a possible solution of the problem.

2. RESEARCH METHODS AND DATA

The methodology was implemented in three stages:

- 1) Field works;
- 2) Laboratory analysis;
- 3) Statistical evaluation of the obtained results; comparison with and interpretation of results obtained by other researchers using different investigation methods.

The first and third stages of investigation of carbonate content in glacial and non-glacial deposits bear differences whereas the second stage in both cases is identical (Fig. 2.1).

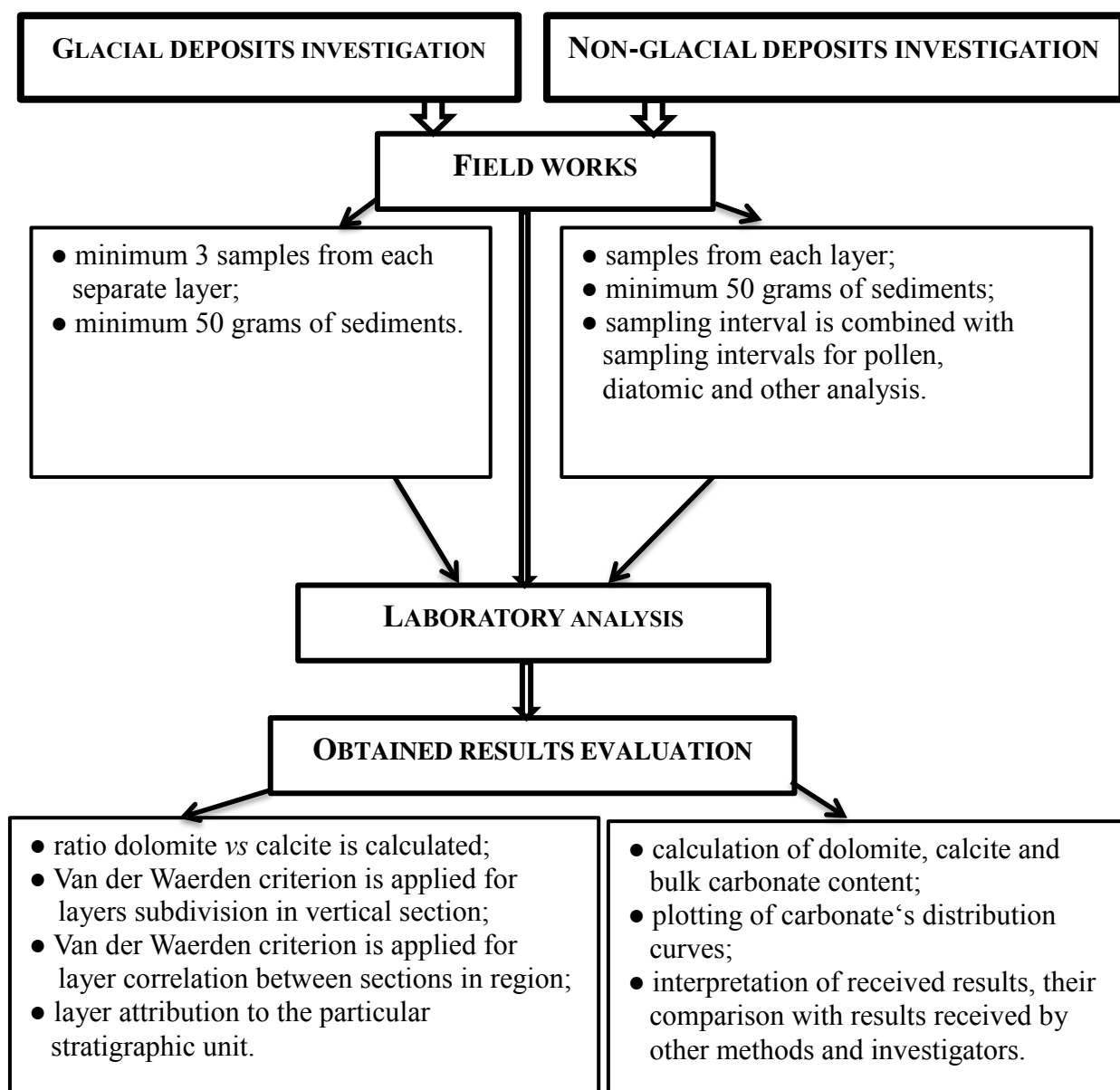


Fig. 1. Methodological scheme.

2.1. Analysis of thin sections of Pleistocene tills and examination by SEM

Searching for potential lithostratigraphic criteria in the fine clastic material of Pleistocene tills (<1 mm) a preliminary analysis of microstructure and composition of thin sections of till was performed. The thin sections of tills were cut from till monoliths of Jurkonys-51, Neciūnai-44 and Žalioji-48 (Southeast Lithuania) (Fig. 2.) sample cores and examined using polarized microscope ECLIPSE E200. Eighteen thin sections of tills were examined.

In order to determine the mineral composition of carbonates and to estimate the proportions of clastic carbonates, which got into till from the glacier bed during exaration, and, possibly, epigenetic carbonates, the fine-grained portion of tills (fraction <1 mm) was examined using scanning electron microscope (SEM). By author's request, the tills from borehole Laukžemė-3 were analysed by E. Starnawska at the Laboratory of the National Research Institute, Polish Geological Institute, and the tills from the Kauno Marios outcrops by L. Šiliauskas at the Nature Research Centre (NRC) using backscattered electron images (SEM-BSE).

Preparation of thin sections of till is a complex and rather expensive procedure. Microscopic examination of thin sections is a time-consuming method. The same is true about till examination by SEM. Therefore, the author sought for cheaper, less time-consuming and, most important, quantitative research method, which would allow distinguishing potential lithostratigraphic criteria for further investigations. Eventually a calcimeter was chosen, which could help to determine the content of carbonate class minerals and bulk content of carbonates.

2.2. Analysis of carbonates in glacial tills

At the stage of **field works**, samples were taken from deep boreholes through the entire Quaternary thickness, shallow (up to a depth of 25–28 m) cartographic boreholes and outcrops. Not less than three samples were taken from every till layer taking into account visual differences of the intervals of till sections. Each sample weighted no less than 50 g.

Laboratory analysis. After evaluation of the chemical method for determining carbonate content, suggested by M. Eidukevičienė (1979), the author decided to use V. N. Ščerbina's method (Щербина, 1958), which, as distinct from other calcimeters, allows determining not only calcite but also other carbonate minerals.

In order to use the mentioned method, certain modifications and calibrations had to be performed: the formula of calibration coefficient calculation was amended (Рудницкайте, 1980) and the methodology for determining bulk content of carbonates and content of individual carbonate minerals (Рудницкайте, 1980; 1981; 1982; 1987; 2006; Гайгалас, Битинас, Рудницкайте, 1985, and others) was improved. The author sought to reduce the investigation time without affecting the accurateness of obtained results, i.e. the method had to become an “express” method. The accurateness of the obtained results was evaluated by colleagues, who performed a comparative analysis of results obtained from the same samples but by different methods (Safarevič, 2006; Šostak, 2006; Kaminskas, 2006).

This analytical method is based on a well-known fact that the reaction of calcite and dolomite minerals to 5% HCl is different. The investigated samples are exposed to hydrochloric acid fixating the release of CO₂ from carbonate minerals during a certain time span.

It is known that during the first 30 seconds the powdered material exposed to 5 ml of 5% HCl at room temperature releases CO₂ from calcite and later from dolomite. After heating the sample to 40°C for three minutes, CO₂ is fully released from dolomite.

The influence of meteorological conditions (atmospheric pressure and air temperature) on the accurateness of measurements is eliminated by introduction of calibration coefficient. Before the procedure and after every 5 examined samples, the release of CO₂ from 0.2 g of pure calcite is measured with the same calcimeter (2–3 control measurements). The volume of CO₂ released during the first 30 seconds is fixated. The calibration coefficient is calculated using formula:

$$K = 44 / x,$$

where:

K – calibration coefficient;

44 – CO₂ volume released from 0.2 g of pure calcite on the day of framing the calcimeter scale;

x – CO₂ volume determined by control measurement.

For determining the carbonate content a fine (<1 mm) sediment fraction is used which is isolated by screening and then powdered. For analysis 0.3 g of the powder is taken. Every sample undergoes 5 measurements and the average values of CO₂ are logged and used for further calculations.

The volume of CO₂ released from every mineral is multiplied by the coefficient of the empirical mass of the mineral deriving the mineral percentages. For calcite, the coefficient is 2.273 (CO₂ versus CaO in mineral is 1 : 1.273; for dolomite it is 2.088 (CO₂ vs CaO vs MgO is 1 : 0.635 : 0.453). In this way, the percentages of calcite and dolomite contained in a sample, bulk content of carbonates and the ratio between calcite and dolomite are determined.

At the stage **evaluation of obtained results**, homogeneity of till layers in the vertical sections of boreholes and outcrops was checked according to dolomite and calcite ratio and using statistical methods. Subsequently, the layers distinguished in the vertical sections were collated with the layers of different boreholes or outcrops. This procedure allowed determining the spatial distribution of till layers with most comparable composition of carbonate minerals.

As the number of samples taken from the compared distributions – till layers – differs and the data distribution pattern is unknown, Van der Waerden criterion was chosen for correct statistical evaluation.

The nonparametric Van der Waerden criterion (X criterion) is used when distribution of samples in the compared bodies is low and uneven or when the average values are derived from semi-quantitative data, or when the distribution pattern is unknown.

The verification of the hypothesis about the compatibility of average values of two data sets (A and B) by Van der Waerden criterion begins with the ranging of the values of both data sets, i.e. arrangement of values in a row in increasing values.

$$X = \sum_1^h \psi\left(\frac{i}{n+1}\right),$$

where n – total number of both sets of samples; h – number of samples in the data set B; Ψ – the inverse function of normal distribution.

If in $n > 20$ the X value is distributed asymptotically with mathematical probability 0 and dispersion $\sigma \frac{2}{x}$, verification procedure of a hypothesis includes calculation of the values of argument $i/(n+1)$, finding values of function Ψ for these arguments from the tables of the inverse function of normal distribution, summing up of the values of function Ψ and comparison of the obtained value of X criterion with the values from the table for number of samples n and difference between A and B data sets. If the calculated absolute X value exceeds the value given in the table the hypothesis about the compatibility of average values is dismissed (Каждан, Гуськов, 1999). This calculation procedure requires much “handwork”. Unfortunately, Van der Waerden criterion is not included in the statistical packages. Using SAS program (Levulienė, 2009) the obtained result is in the form of P value. This Statistical Analysis System, containing the highest choice of algorithms among the professional data analysis systems and intensively elaborated since 1976, in its version SAS 6.11 introduced calculation of accurate P values (used when distributions are small or incompatible; when the law of data distribution is unknown) for Van der Waerden criterion. This version was released in 1997 (Levulienė, 2009; Rudnickaitė, 2008; 2013; Rudnickaitė et al., 2015). At present, the result is obtained using version SAS 9.4.

A hypothesis is accepted when two distributions (X and Y) according to the ratio of dolomite and calcite are compatible with significance level 0.05. When P value was lower than 0.05, a hypothesis was dismissed, i.e. distributions were regarded as statistically incompatible. This means that till layers were different.

1.3. Analysis of carbonates in non-glacial sediments

Analysis of carbonates in non-glacial sediments also took three stages (Fig. 2.1.).

During the field works, samples were taken from every layer with different lithology. The section of the outcrop, borehole, pit, etc. was described *in situ*. The interval of sampling was matched up with the sampling intervals for pollen, diatomic and other analyses. The total weight of discrete sample had to be sufficient for all planned

analyses. Not less than 50 g of sediments were examined for carbonate content. When no other investigations are planned samples are taken every 5 or 2 cm.

Laboratory analysis is identical for all genetic types of sediments (Fig. 1.). Therefore, the non-glacial sediments were analysed in the same way as tills.

During the **evaluation of the obtained results**, the data were processed using Microsoft Office Excel programme. Through the medium of this programme, calcite and dolomite quantities were calculated, vertical distribution curves of carbonates drawn, the curves correlated with the lithological composition of investigated sections, the obtained results interpreted, palaeogeographical conditions of sedimentation described, and the obtained results compared with the results obtained by other authors using different research methods.

2.4. Research material

The material was collected during field trips from outcrops. The samples of cores were taken from core storage. Some samples were procured from other researchers: A. Gaigalas, O. Kondratienė, A. Bitinas, A. Damušytė, V. Šeirienė, M. Stančikaitė, R. Guobytė and others, who have investigated Pleistocene deposits by other methods. The latter circumstance strongly facilitated collation of the obtained data.

The investigated material was divided into two groups according to genetic features: glacial deposits (tills) and non-glacial sediments (mainly limnic, aeolian and sometimes of oxbow lakes).

Thin sections of tills were cut from the cores of Jurkonys-51, Neciūnai-44 and Žalioji-48 boreholes. The fine-grained (<1 mm) fractions of tills analysed by SEM were analysed in the samples from Laukžemė-3 borehole and Kauno Marios outcrops.

In order to achieve the objective of the present study and to fulfil the tasks, the samples were taken from heterochronous tills in different parts of Lithuania (Fig. 2.). Samples were taken from ~120 vertical sections of boreholes and outcrops and ~2600 samples were analysed. The number of carbonate measurements, including control ones, was five times as high.

Heterochronous non-glacial sediments were investigated from the known interglacial sections of the Lithuanian Quaternary sediments (Snaigupėlė-705 borehole

and outcrops of Butėnai, Valakupiai and Meilės sala, Netiesos and Jonionys ravines, etc.) and Late Glacial and Holocene sections (boreholes 65a, Šventoji port, Smeltė-90c, Nida-VI, Lopaičiai 2, Pakastuva, etc., and outcrops Dūkštos III, Dubyčiai I and II, Mūša Tyrelis, Zakeliškės, Dengtiltis, Krokšlys, Ventės Ragas, etc.).

The total of ~2300 samples were analysed whereas the number of performed measurements was five times as high.

3. RESULTS

3.1. Quantities of carbonates in the Pleistocene tills

3.1.1. Carbonates in tills according to the data of thin section analysis

The preliminary stage of search for potential lithostratigraphic criteria in the fine-grained (<1 mm) fractions of tills included investigation of mineral composition of this fraction in thin sections of tills cut from the cores of Jurkonys-51, Neciūnai-44 and Žalioji-48 (Southeast Lithuania) (Fig. 2.).

This sub-section contains a general description of thin sections of tills grouped according to the bedding depth and similarities of colour, structure and texture and presumable belonging to till layer of the same age.

Till bedded in *boreholes Neciūnai-44 (depth 126.8–135.0 m) and Žalioji-48 (depth 71.4–75.1 m)* resembles polymictic badly sorted sandstone. Grains of clastic material in the main cementing mass account for 60–70 %. Till cement is contact-basal, accounting for 30–40 %, polymictic, composed of powdered carbonates and clay minerals. The size of the cementing particles ranges from especially thin dispersed to aleuritic.

The clastic material mainly is represented by sand-aleurite fractions and, in rare cases, by disorderly distributed gravel–pebbles. Sometimes parallel arrangement of elongated fragments can be observed, which reflects the direction of advancing glacier. Strips of especially fine grains engirdle some coarser fragments.

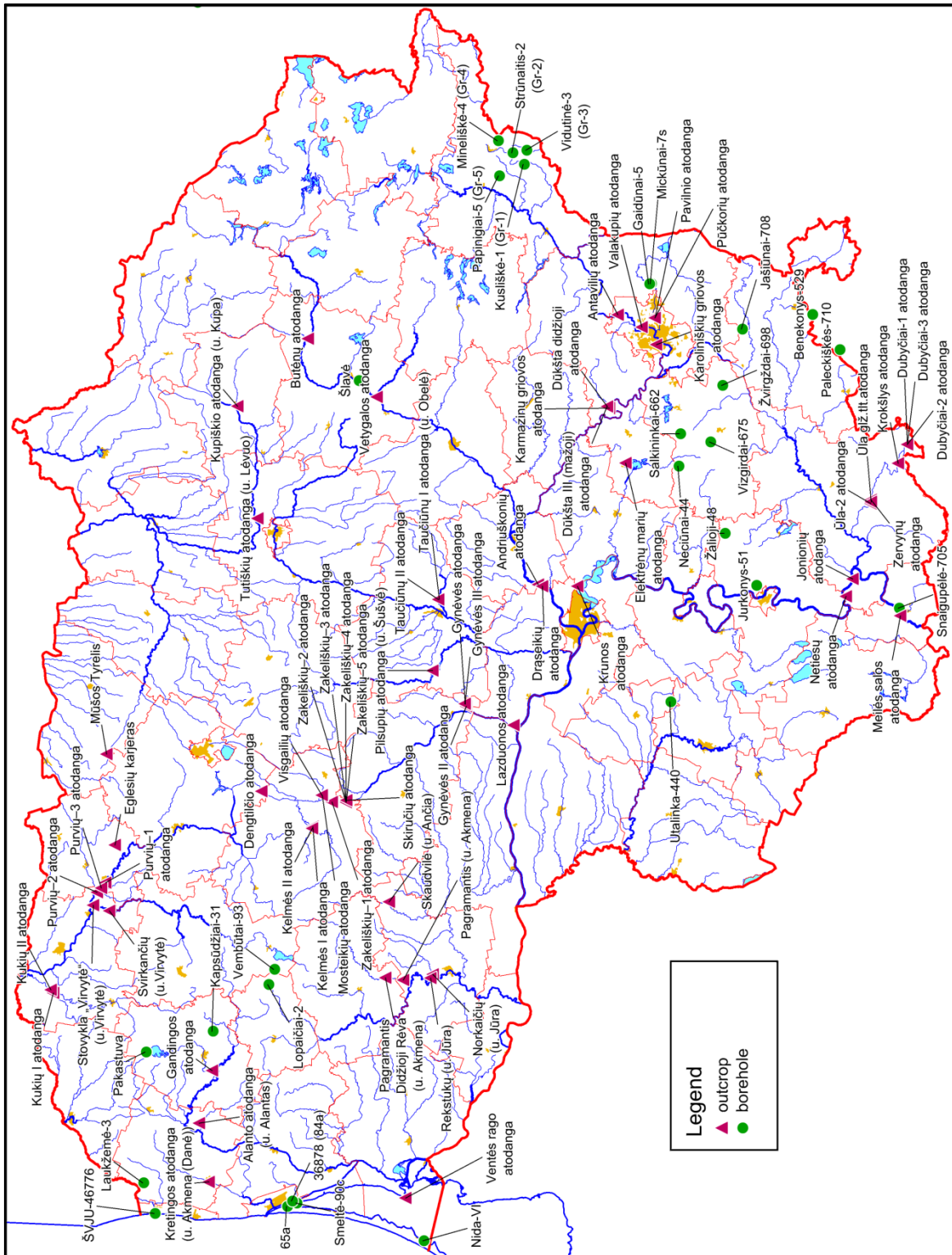


Fig. 2. Distribution map of the investigated vertical sections.

All sand and aleurite fractions are predominated by quartz grains (60–80 %), which are better polished in coarse fractions. The portion of polished grains accounts for up to 50 %. Aleuritic fraction-sized quartz grains bear almost no traces of polishing; grains with sharp angles are dominant. Also can be found fragments of carbonaceous rocks (5–15 %, feldspars (5–10 %) and crystalline rocks (10 %), and isolated grains of chalcedony, glauconite, mica, black ore minerals, amphiboles, pyrite and marcasite, garnet and other minerals.

Gravel and coarse sand fractions more often contain fragments Palaeozoic and Mesozoic limestones, sandstones, aleurolite, chalk, marl, and, rarer, dolomite. The older rocks are represented by pre-Cambrian garnets, gneisses, quartzites, diabases, gabbro, etc. Also can be observed fragments of dense porphyry and amphibole-plagioclase porphyry. Some clastic material of crystalline rocks is strongly weathered.

The analysed till is distinguished for higher portion of sand, relatively high content of local Mesozoic debris, grey colour, *calcitic composition of pelitomorphous material* and noticeably higher density.

The till from *boreholes Jurkonys-51 (depth 64.3–82.4 m) and Žalioji-48 (depth 53.6–65.8 m)* like other tills is composed of moraine loam with pseudo-psammite-aleuropelite structure. In comparison with the above described one, this till contains **greater amounts of dolomitic pelitomorphous impurities** and red clayey aggregates in the cementing flaked hydromica mass. The contact-basal cementing material accounts for 30–40 % of the rock mass. It is composed of polymictic polymineral badly sorted material of ground sedimentary and crystalline rocks. The bulk mass of the till is coloured brown by iron hydroxides. Some patches are strongly limonitized. The elongated fragments are arranged in parallels corresponding the linear arrangement of micro fissures.

The relict grains of different size in the fine-grained till mass account for 60–70 %. Medium (diameter from 0.5–0.25 mm) and fine (diameter from 0.25–0.1 mm) sand fractions are dominant. The grains are composed of quartz (60–70 %), carbonaceous minerals and rock debris (6–25 %), feldspars (5–15 %), crystalline rock debris (3–15 %), sandstones (3–6 %), and micas. The relict grains are poorly polished. Some of them are crushed and surrounded by finer fragments. A small part of quartz grains is distinguished by ideal inherited polishing. The quartz grains are variable in size,

with wavy surface. Clean, transparent quartz grains without fissures occur. The brittle feldspars are poorly polished. The clastic material includes abundant fragments of Palaeozoic dolomites, sandstones, rapakivi, argillite and other rocks. The fragments of carbonaceous rocks as a rule are well polished. The accessory part contains amphiboles, garnets, magnetite, ilmenite, epidote, pyrite, marcasite, glauconite and other rare minerals.

The till from boreholes *Jurkonys-51 (depth 49.0–60.95 m)*, *Neciūnai-44 (depth 109.8–117.0 m)* and *Žalioji-48 (depth 34.8–47.6 m)* contains greater amounts of clayey particles than the above described till. It represents morainic loam transitive to boulder clay. The cement is of basal type, hydromicous, with impurities of finely crushed dolomite powder. The bulk mass of the till is reddish brown due to abundance of especially thin dispersed iron hydroxides and ferruginous ochre. 40–50 % of the till are composed of especially thin dispersed mass and 50–60 % of relict clastic material. Aleuritic-gravel sized quartz grains account for 60–70 % of the latter. Quartz grains with wavy surface split away from the crystalline rocks occur in abundance. Their polishing worsens with decreasing size and disappears in the aleurite fraction. Feldspars account for 10–20 % and are represented by microcline, orthoclase and acidic and of medium composition plagioclases. Potassium feldspars are strongly pelitized. The rock debris contains large amounts of dolomites, crystalline lime, garnets, rapakivi, microquartzites, diorites, gabbro, plagioclase porphyrites, sandstones, hornfels, etc. Palaeozoic dolomites are dominant among carbonate minerals and mineral debris accounting for 10–20 %. ***Isolated fine dolomite rhombohedrons formed by crushing of dolomite rocks stand out in the bulk mass of till.***

The clay particles of the bulk mass are of brown colour, microscaled. Somewhere, the isolated grains of clastic material are enveloped by hydromica membrane. There are occurrences of compacted or ferruginous formations of deposits with blurred boundaries.

Tills of this group are distinguished from the above described ones for high quantities of dolomite, clayey texture, weathered upper section, reddish brown colour of various intensity and optimal mixture of badly sorted fractions.

Half of the till from *borehole Neciūnai-44 (depth 0.0–6.7 m)* is composed of sand, gravel and abundant clastic material. The other part is composed of especially thin dispersed bulk mass. The cementing material is of different shades of grey, sometimes

with greenish or bluish touch. It is of different degree of crystallization and contains large quantities of hydromica with kaolinite and montmorillonite impurities. ***Carbonaceous (usually calcitic) minerals and opal and microorganism nodules occur in the bulk mass of till.***

The clastic material of till is badly sorted. Gravel and coarse sand grains are comparatively well polished. Fine and coarse sand fractions with poorly polished grains are dominant. The grains of sand fraction are mainly composed of quartz (75–80 %), feldspars (5–10 %) and carbonates (10–15 %). They also have fragments of crystalline rocks (garnet is dominant), sandstone, flint, marl, phosphates, glauconite and other rocks and minerals. Somewhere, there are occurrences of black Jurassic aleurolites and sandstones. The coarse sand and gravel fractions have elevated quantities of lime, crystalline rocks, marls and other rocks (up to 60–80 %). Accessory rare mineral in sand and aleurite fractions are amphiboles, garnets, pyrite, marcasite, magnetite, ilmenite, rutile, zircon, etc.

The described till ***is distinguished for elevated quantities of debris of Mesozoic marls and other rocks, content of Palaeozoic organogenic limestone and elevated portion of clayey.***

3.1.2. Morphology and genesis of carbonate minerals in tills

Visual analysis of the mineral composition of fine-grained portion of tills and morphology of minerals and rock fragments (Figs 3–4.) in thin sections of tills using polarised microscope ECLIPSE E200 suggest a conclusion that carbonates in the glacial deposits formed in the process of crushing and disintegration of rocks eroded from the glacier bed.

Till samples taken from different depths of Laukžemē-3 (Fig. 2.) borehole were grouped into fractions according to granular composition (Table 3.1.2.1.). Thin dispersed portion (fraction $\varnothing < 1$ mm) of tills was chosen for further analysis using SEM.

The aim was to determine the mineral composition of carbonates and to identify their genesis. SEM with different analysers provides this possibility (Krinsley et al., 1998; Robinson & Nickel, 1983; Reed, 2005; Watt, 1997, and others).

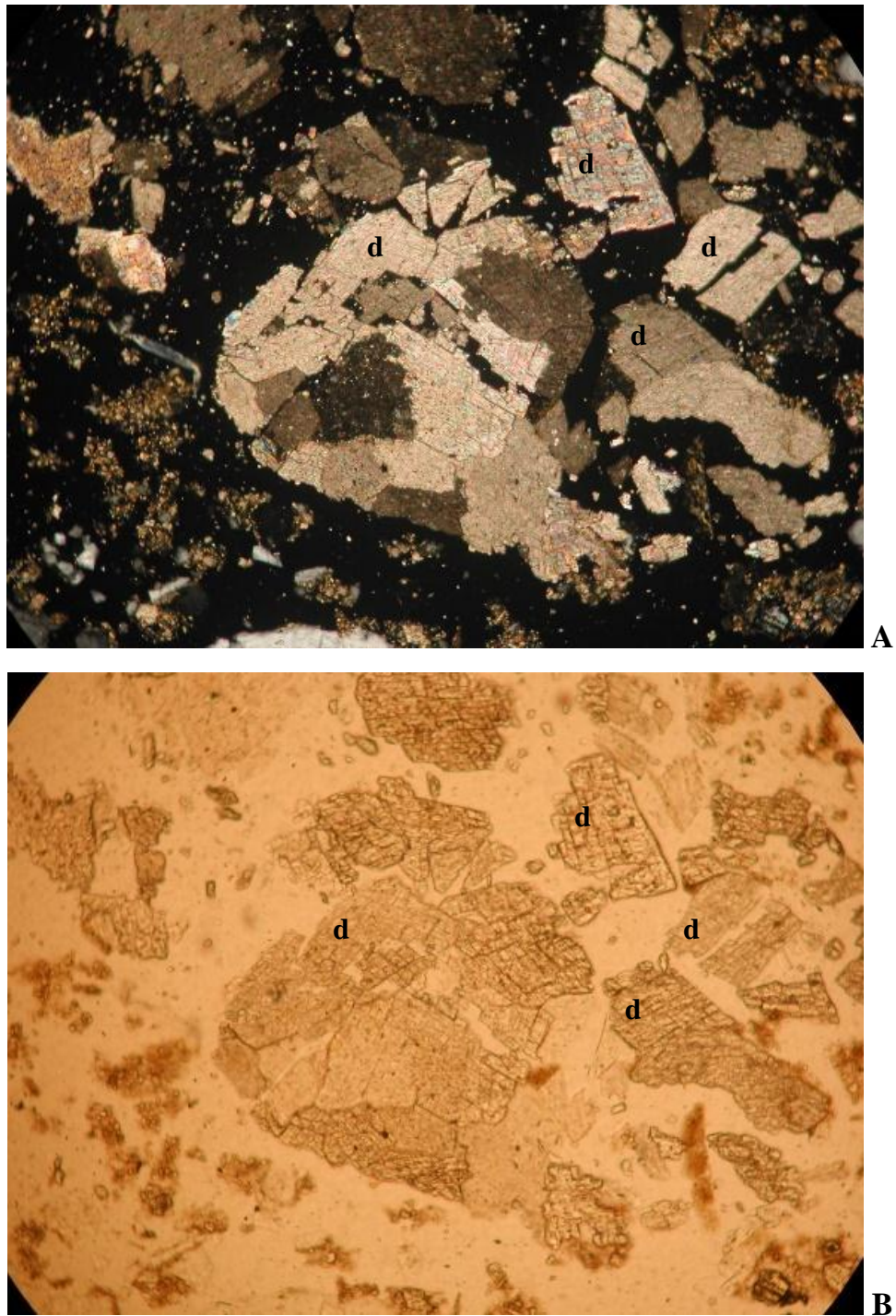


Fig. 3. Crumbles dolomite (d) crystals, dark mass – mixture of clay minerals and thin dispersed calcite. Borehole Žalioji-48, depth 65 m, X 10. A – image with crossed nicols.¹

¹ Photos of tills thin sections was made using polarised microscope ECLIPSE E200 at VU department of Geology and mineralogy of Vilnius University. Horizontal length of the each photos border is 2.5 mm.

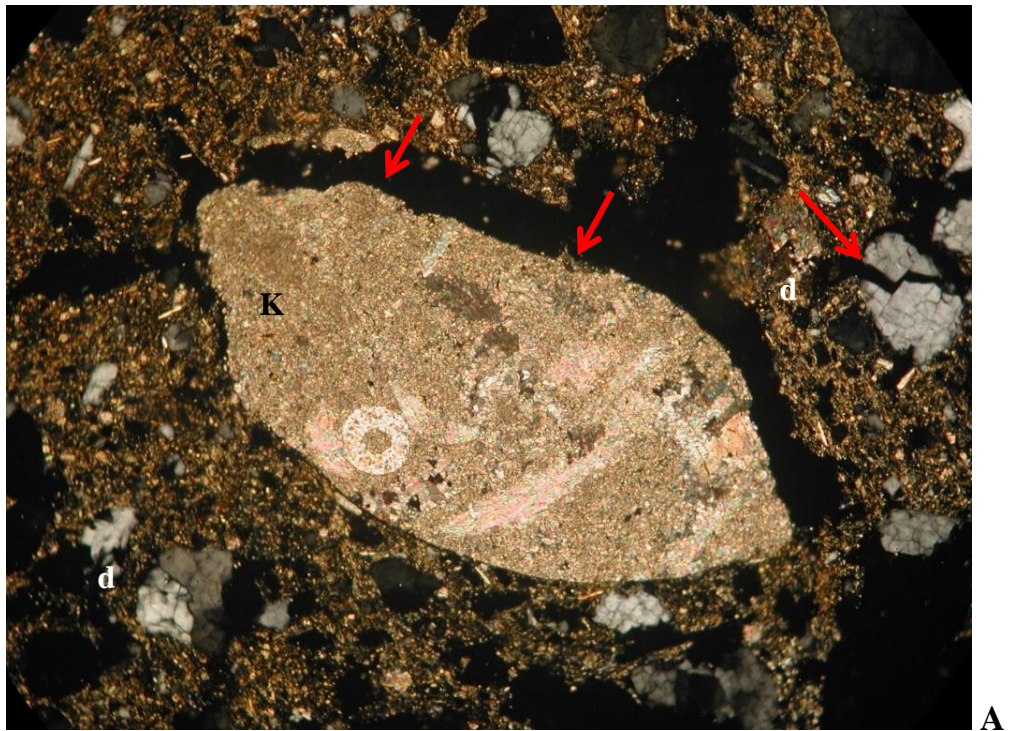


Fig. 4. Signs of microdislocation (red arrows) near limestone (K) pebble and dolomite (d) crystal. Borehole. Žalioji-48, depth 36.8 m, X 10.

A – image with crossed nicols

Table 3.1.2.1. Sampling depths and techniques used for analysis of till samples from borehole Laukžemē-3

No of till layer	Depth, m	Lithological description	Sample No	
			Identification of minerals by SEM EDS ($\varnothing < 0.1$ mm)	Analysis by SEM, SE image ($\varnothing < 0.1$ mm)
1	3.0	Morainic loam, yellowish brown	1-4	1-1; 1-2; 1-3; 1-5
2	4.3	Morainic sandy loam, brownish grey with yellow (tobacco) patches	2-5 2-6	2-1; 2-2; 2-3; 2-4; 2-5; 2-6
3	6.0	Morainic loam, grey–dark grey to brownish grey	-	3-1; 3-2; 3-3
4	11.3	Morainic loam, grey–dark grey	4-1	4-1; 4-5
5	33.7	Morainic loam, grey	5-2	5-2
6	38.0	Morainic loam, brown with grey shade	6-2	6-1a; 6-4a

The mineral composition of tills was determined according to the energy dispersion spectrum using SEM EDS.² The obtained curves show that the thin dispersed portion of till contains feldspars (Fig. 5.), dolomite (Fig. 6.), dolomite with clay mineral impurities within crystal (Figs 7.), calcite (Fig. 8.) and clay minerals. The latter occurs as an impurity in both the examined dolomite and calcite. Presumably, clay minerals are not within mineral crystals but on their surface.

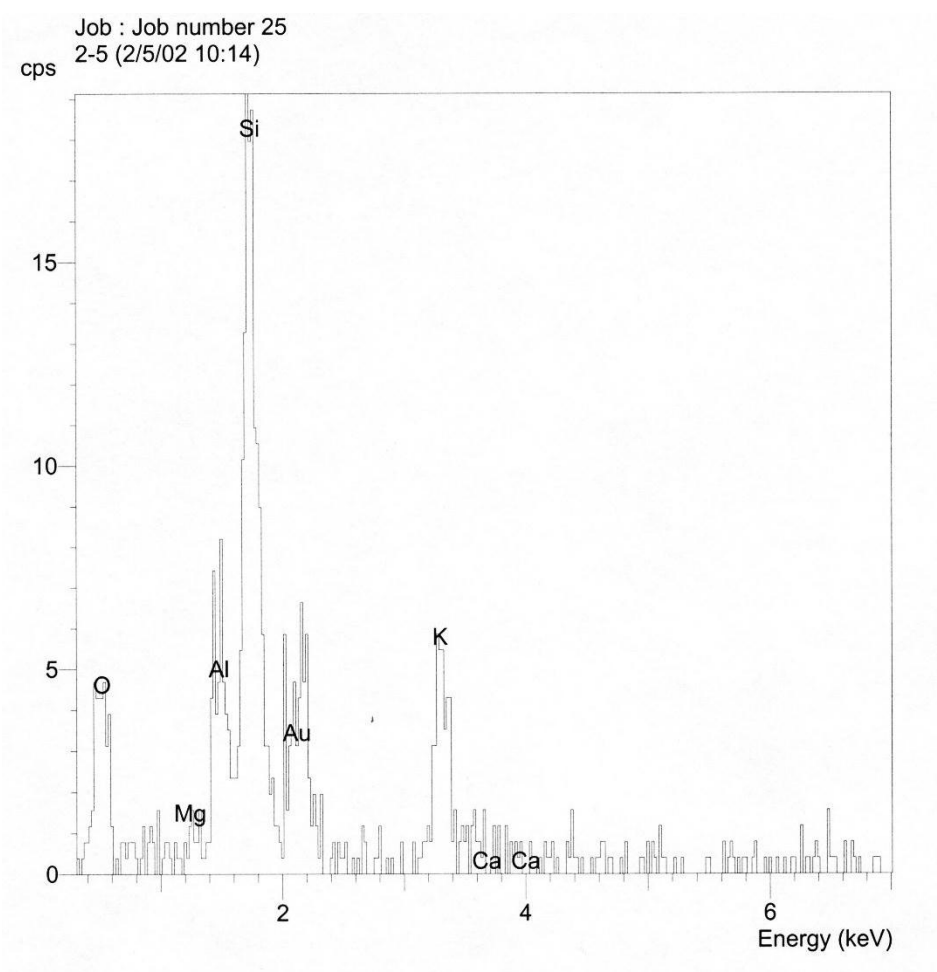


Fig. 5. *The determined feldspar (sample 2–5).*

² Analysis was performed by Mgr. E. Starnawska at the Laboratory of the National Research Institute, Polish Geological Institute.

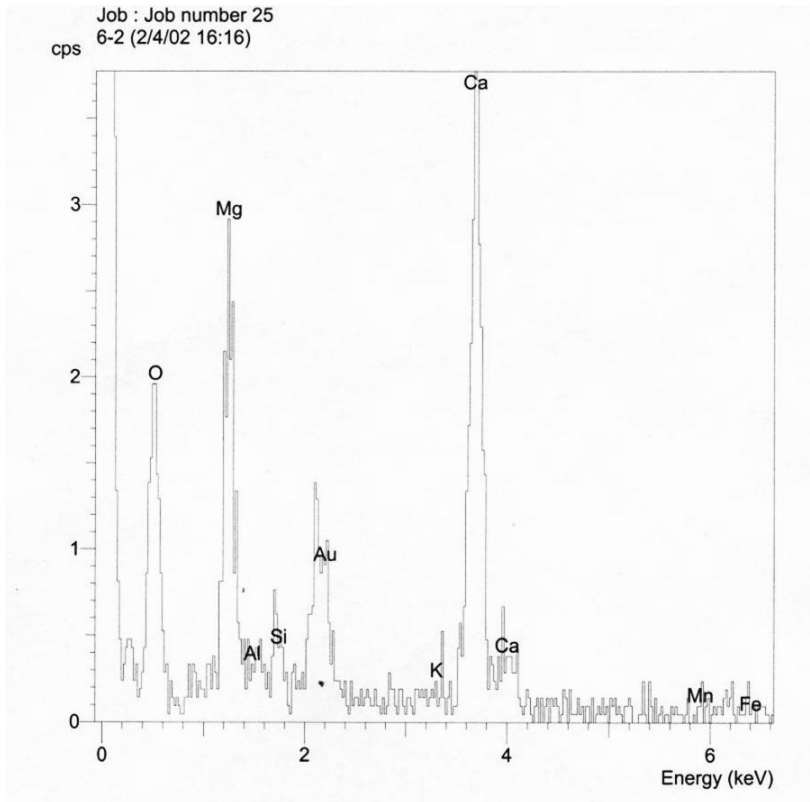


Fig. 6. The determined dolomite (sample 6-2).

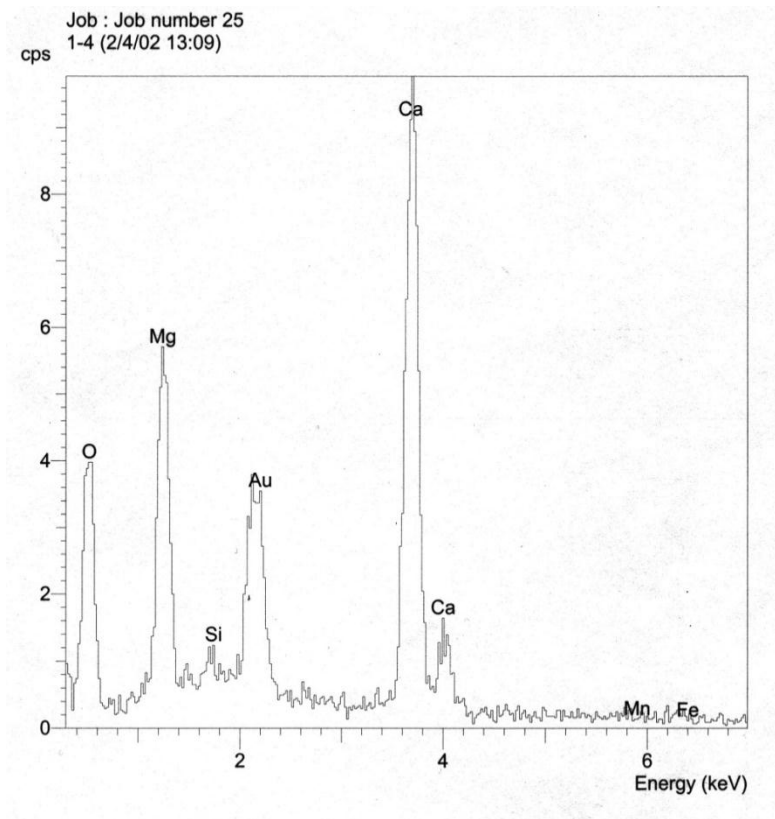


Fig. 7. Dolomite with impurities of clay minerals within crystal (sample 1-4).

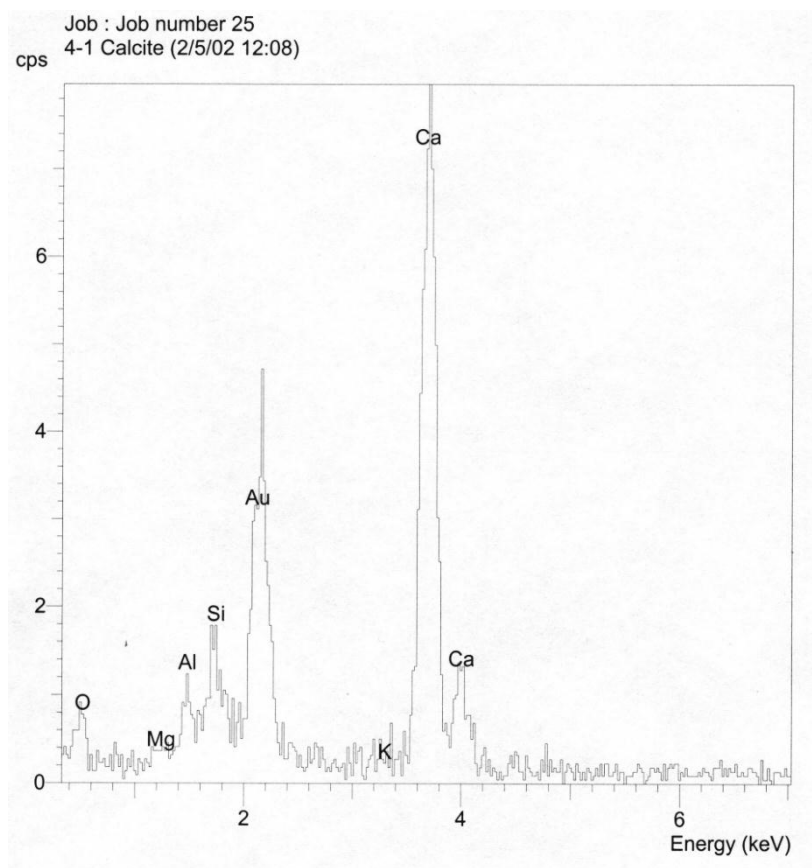


Fig. 8. Calcite (sample 4-1).

Examination of the images of thin dispersed (fraction $\varnothing < 0.1$ mm) portion of tills from borehole Laukžemė-3 using SEM SE³ showed that the absolute majority of identified carbonates (both calcite and dolomite) are clastic material, which got into the till in the process of glacier bed exaration (figs 10–12). No epigenetic carbonates were identified. Carbonate crystals with undamaged walls were absent.

The obtained results are in conformity with the results obtained by other researchers (Aber J. (1979); Lavrushin J. A., Golubev J. K. (Лаврушин, Голубев, 1980); Lavrushin J. A., Geptner A. R., Golubev J. K. (Лаврушин, Гептнер, Голубев, 1986); Fairchild I. J. & Spiro B. (1990); Sharp M., Tison J. L. & Fierens G. (1990); Fairchild I. J., Bradby L. & Spiro B. (1994); Hall J. S., Mozley P., Davis J. M. & Roy N.D. (2004); Rattas M., Lomp P. (2008); Rattas M., Lomp P. & Jöeleht A. (2014)), who maintained that carbonate minerals in glacial sediments formed at the till interface with glaci-fluvial deposits cementing the latter and forming glaciodyke and glaciodyke

³ Analysis was performed by Mgr. E. Starnawska at the Laboratory of the National Research Institute, Polish Geological Institute.

conglomerates or sandstone columns. As a rule, this process usually took place in the areas of end moraines.

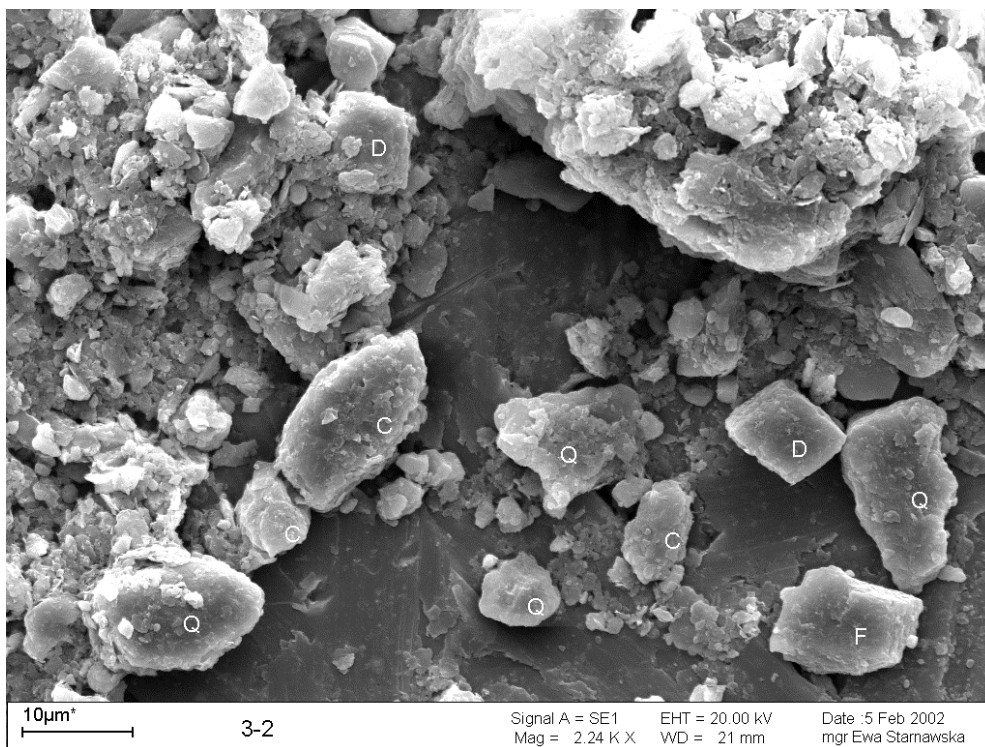


Fig. 10. Identified calcite (C), dolomite (D), quartz (Q), and feldspar (F) grains. All of them bear marks of crumbling, polishing and scraping (sample 3–2).

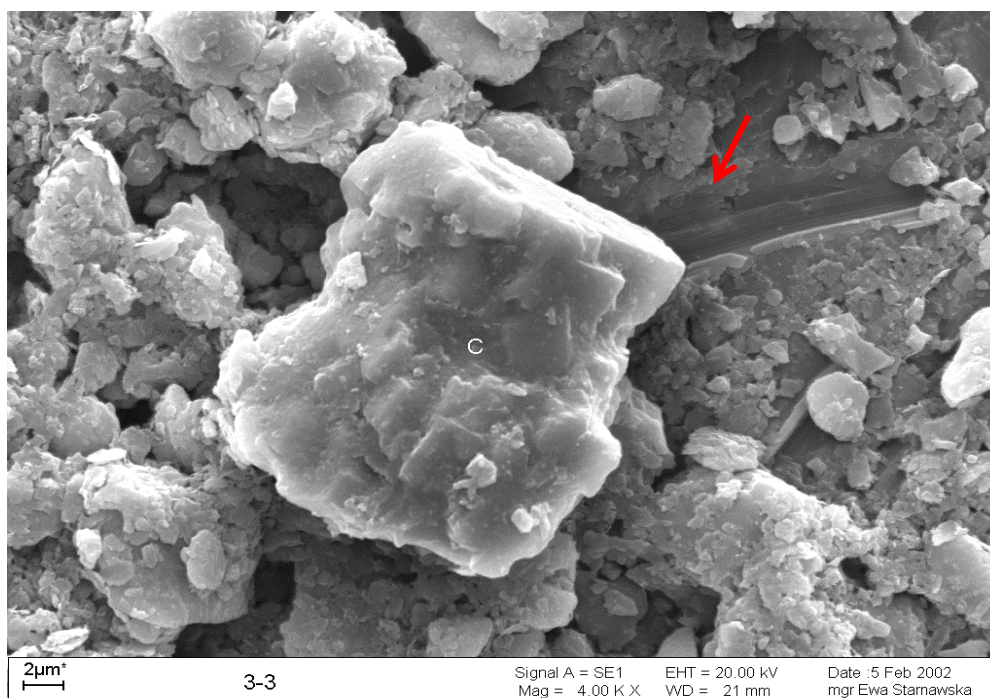


Fig. 11. Calcite grains (C) are more severely broken; gliding mark is visible (red arrow), (sample 3–3).

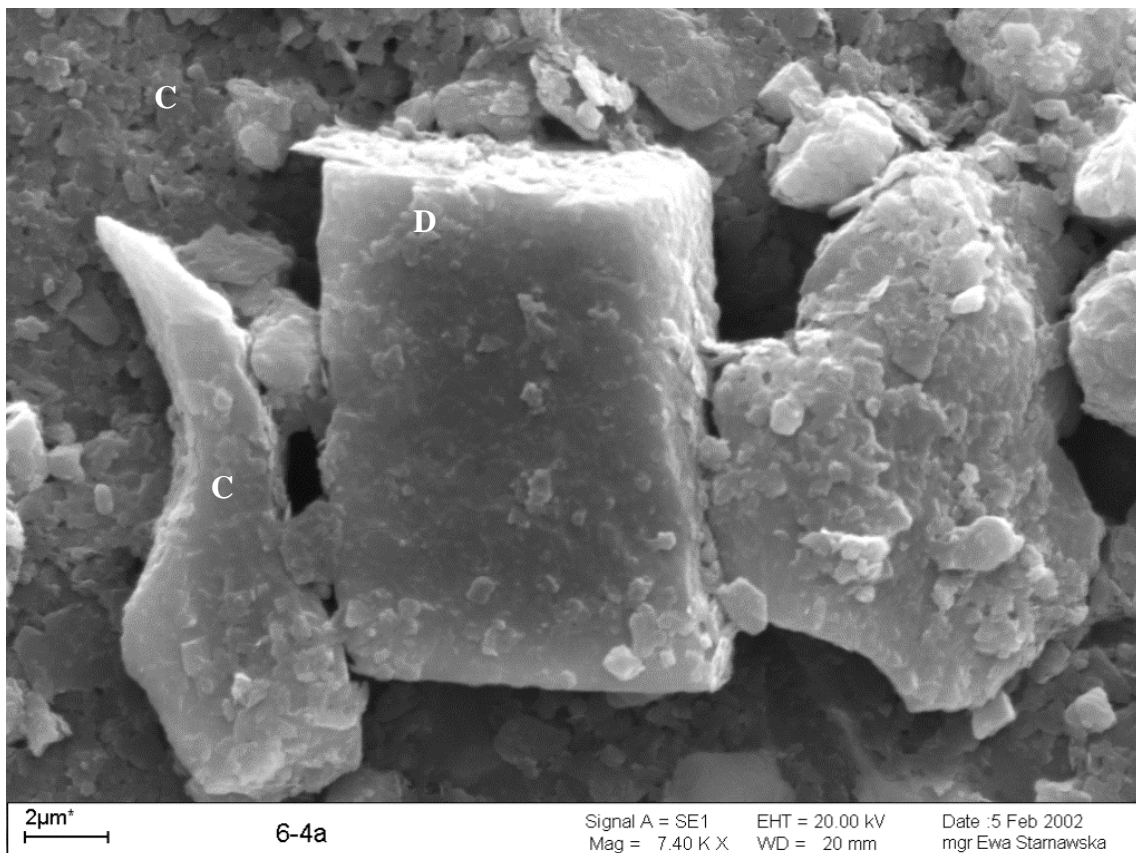
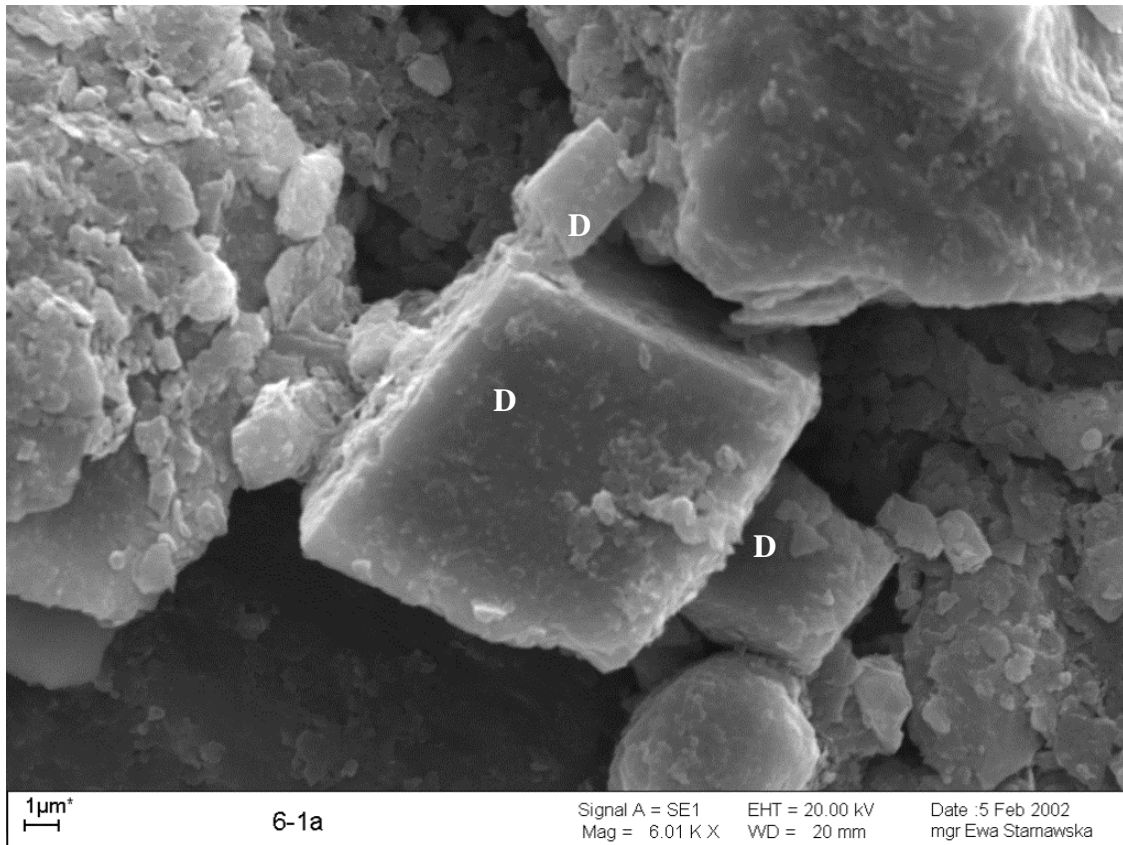


Fig. 12. Crushed dolomite (D) splits into smaller rhombohedrans (sample 6-1a). Calcite grains (C) split into sharper fragments forming thin dispersed mass (sample 6-4a).

The results obtained by examination (using SEM-BSE⁴) (Robinson & Nickel, 1983; Krinsley et al., 1998, and others) of thin sections of tills (not divided into fractions) from Kauno Marios outcrops also confirm the clastic origin of carbonate minerals (Fig. 13–14).

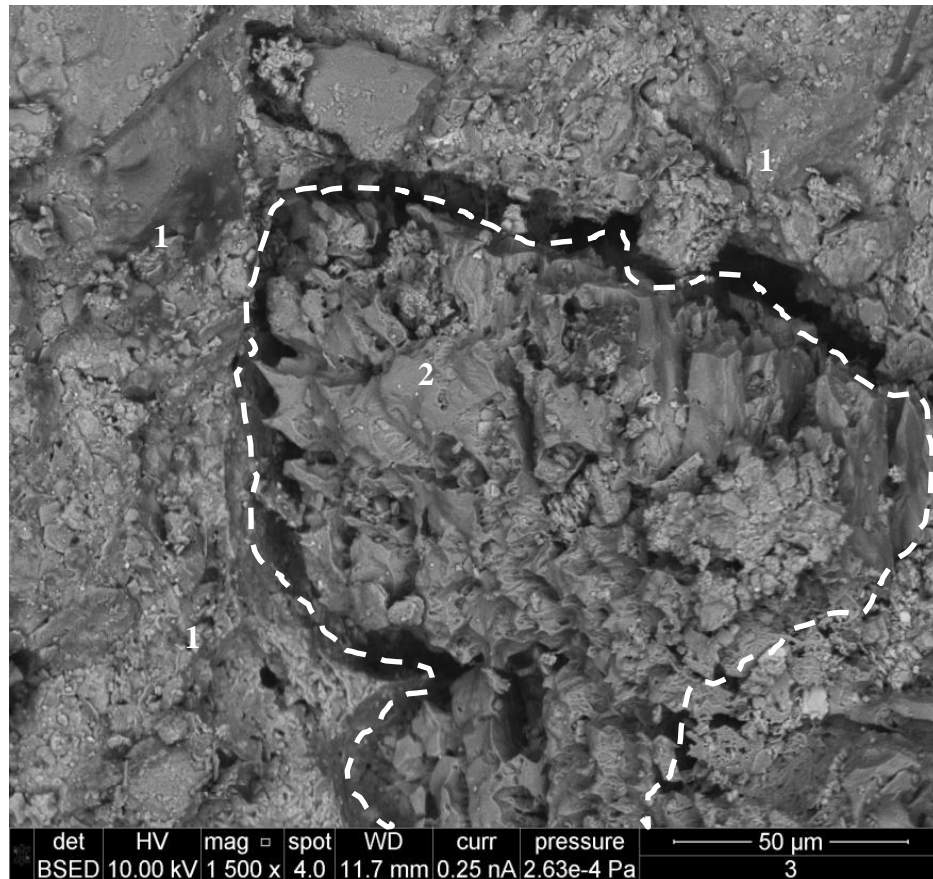


Fig.13. Carbonate minerals in till fraction $\varnothing < 1\text{ mm}$; SEM-BSE image:
1 – mixture of clay minerals and calcite; 2 – broken dolomite pebble.

⁴ Analysis was performed by L. Šiliauskas using free access SEM at the Nature Research Centre.

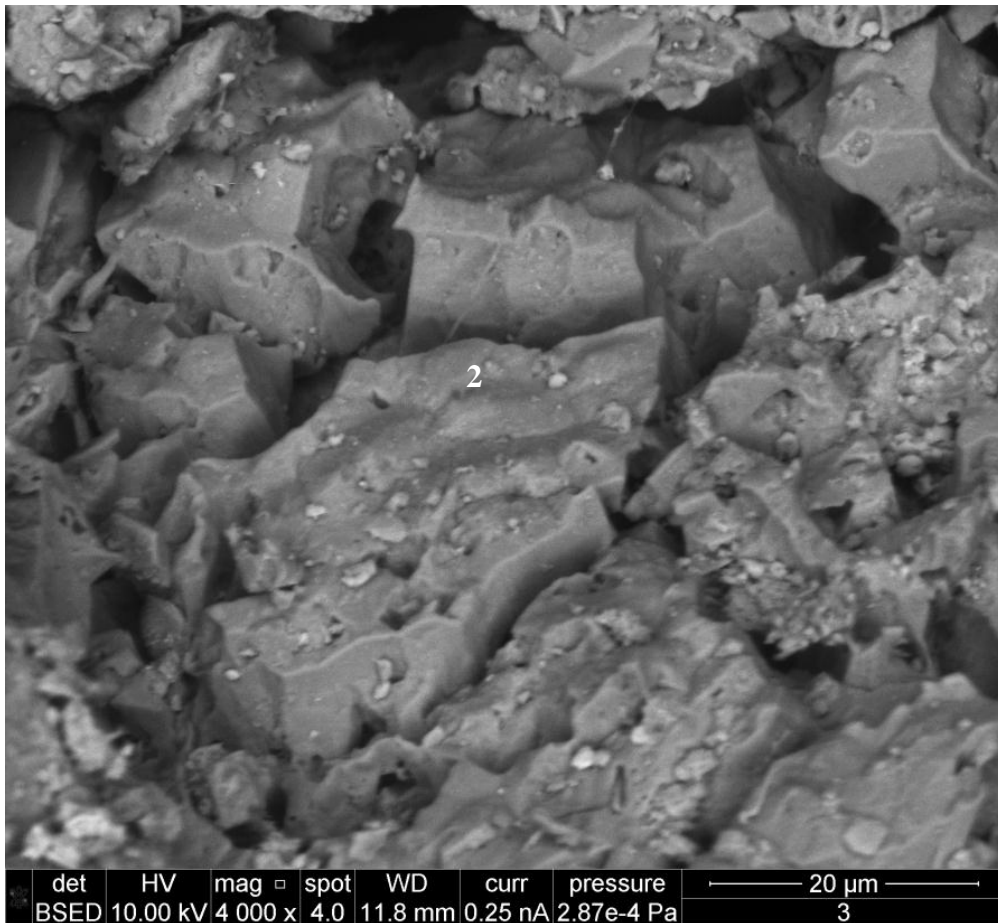


Fig. 14. Magnified SEM-BSE image of broken dolomite pebble (2).
Cleavages are visible.

The data about mineral composition of thin dispersed portion of till and forms of discrete mineral crystals, obtained at the first stage of investigation, allow maintaining that the fine fraction of tills (<1 mm) is composed of clastic material. All examined samples contained clasts of carbonate minerals dolomite and calcite. According to visual examination, their quantities and ratio in till layers different in age (heterochronous) are different and, in our opinion, could serve as a lithostratigraphic criterion.

3.1.3. Distribution of carbonate minerals in heterochronous tills

Carbonate content of the fine-grained (<1 mm) portion of heterochronous tills from boreholes Jurkonys-51, Neciūnai-44 and Žalioji-48 was investigated using

calcimeter. The samples were taken from the same core monoliths from which thin sections were cut for microscopic analysis (Chapter 3.1.1.).

According to the ratio dolomite *vs* calcite, the till horizons in the vertical section were grouped into homogenous different layers using the Van der Waerden criterion. Three layers were distinguished in borehole Jurkonys-51, two in the borehole Neciūnai-44 and four in borehole Žalioji-48.

The layers distinguished visually according to the ratio dolomite *vs* calcite in the vertical sections of the mentioned three boreholes were divided into the following groups: the first layer of borehole Neciūnai-44 with the second layer of borehole Žalioji-48; the second layer of borehole Jurkonys-51 with the second layer of borehole Neciūnai-44 and the third layer of borehole Žalioji-48. The second group is distinguished for higher content of dolomite supporting the trend observed by thin section analysis (Chapter 3.1.1.).

The fourth layer in the vertical section of borehole Utalinka-440 and the fifth layer of Salkininkai-662 borehole, distinguished according to the ratio dolomite *vs* calcite, could also be included in the second group.

The grouping of the vertical distribution of till in boreholes and outcrops according to carbonate content analysis data is illustrated in the examples given below.

Carbonate content analysis of heterochronous till samples from borehole Utalinka-440 across the Quaternary deposits in the southern part of Lithuania showed that:

calcite and dolomite are dominant in the till layers. Their percentage and ratio in heterochronous Pleistocene tills are different. According to the ratio dolomite *vs* calcite (using Van der Waerden criterion) five homogeneous different till layers were distinguished in the vertical section of the borehole.

In the deepest first layer, dolomite accounts for 5.6 % and calcite for 19.2 %. The bulk content of carbonates accounts for 24.8 %. The ratio dolomite *vs* calcite (d:c) is 0.292.

In the second till layer, dolomite accounts for 9.0 to 11.2 % (average 10.3 %) and calcite for 19.6 % to 25.5 % (average 21.9 %). The bulk content of carbonates reaches 34.5 %. The ratio d:c is 0.470.

In the third layer of till, the content of dolomite ranges from 8.6 to 16.2 % (average 11.0 %) and calcite from 19.6 to 25.4 % (average 21.7 %). The ratio d:c is 0.057.

The percentage of dolomite in the fourth layer of vertical till section ranges from 9.4 to 19.8 % (average 15.1 %) and calcite from 10.4 to 19.4 % (average 13.1 %). The bulk content of carbonates sometimes reaches 36.2 %. The ratio d:c is 1.153.

The fifth distinguished till layer is binary, composed of morainic light brown sandy loam and morainic dark brown loam. The lower part of the fifth layer contains from 10.5 to 11.4 % (average 10.95 %) of dolomite and from 12.4 to 14.3 % (average 15.3 %) of calcite. The bulk content of carbonates reaches 31.0 %. The ratio d:c is 0.601.

Salkininkai-662 borehole was drilled in the Baltic marginal formations region (Fig. 2.) with stratigraphically almost complete sections of till. Some time ago, it was investigated with co-authors (Гайгалас, Битинас, Рудницкайте, 1985). Stratigraphic subdivision of heterochronous tills in the zone of marginal formations faces difficulties due to glaciolocations of the older tills in younger layers. In many cases, the vertical sections are interstratified with till and glacioluvial deposits. It is especially difficult to distinguish between the primary bedding tills and their glaciolocated blocks reworked by later glaciers into the upper younger layers. For lending substance to stratigraphic distribution, a complex of features was used for investigation of borehole sections. The data were processed using D. A. Rodionov's programme for subdivision of geological bodies. Carbonate content and dolomite *vs* calcite ratio (d:c) were determined in fraction <1 mm. The boundaries between heterochronous tills were determined by evaluation of dolomite *vs* calcite ratio using Student's criterion (Каждан и др., 1979). These boundaries were in good correlation with the boundaries distinguished by Rodionov's method, using lithological and geochemical investigation data. The results of previous investigations showed that up to six heterochronous Pleistocene till complexes can be distinguished in the marginal zone of the Baltic Marginal Highland.

In the present study, six homogeneous different till layers were distinguished in the vertical section Salkininkai-662 borehole according to dolomite *vs* calcite ratio, using Van der Waerden criterion.

In the first (lower) distinguished till layer, the ratio d:c variation bears pulsing character and reflects clastic structure of till. According to statistical evaluation, the layer is homogeneous.

In the second distinguished till layer the d:c ratio is similar and reaches ~0.9.

In the third distinguished till layer, the dolomite vs calcite ratio is varying. In the lower part, a scale or clast incorporated from the second layer are visible.

In the fourth distinguished layer, the d:c ratio is less varying (average ~0.5–0.6). Erratics incorporated from the third layer are visible.

In the fifth distinguished layer, the d:c ratio considerably exceeds 1; reaches even 2.6. It possibly implies dolomite rock elevation eroded by moving glacier.

In the sixth distinguished till layer, the ratio d:c reaches ~0.8. In the lower part of the layer, a scale incorporated from the fifth layer can be observed.

Generalising it could be suggested that dolomite vs calcite ratio reflects glacioloaction of marginal moraines, i.e. incorporation of older till erratics and smaller clasts into younger layers. This should be kept in mind subdividing till layers in the zone of glacial marginal formations according to lithostratigraphic criteria.

Below follows an example of more extensive investigation conducted in another zone of marginal moraines – Švenčionys Highland. Cores of shallow boreholes drilled in five orographically and geomorphologically different surface areas (Rudnickaitė et al., 2015) (Fig. 2.) were investigated.

The till samples were analysed for carbonate content, CO₂ content released from calcite and dolomite, percentages of dolomite and calcite, and ratio dolomite vs calcite in all 293 samples taken from the cores of the five boreholes.⁵

The determined calcite content in the till of Kusliškės borehole (Gr-1) (Fig. 15.) ranges from nine to 13.5 %, whereas in some samples it reaches 16 %. Dolomite distribution is uneven. Its content ranges from 5 to 10 % in the brown sandy loam. Its percentage in the grey loam is 4 %. In the contact zone between the greyish brown and grey sandy loam, the percentage of dolomite increases to 11 %. It decreases again in the grey sandy loam accounting for 5–9 % across the layer.

⁵ Due to the limited space of the summary of dissertation, the data tables are not given. The full set of results is stored at the author's database.

Gr-1 (185,0)

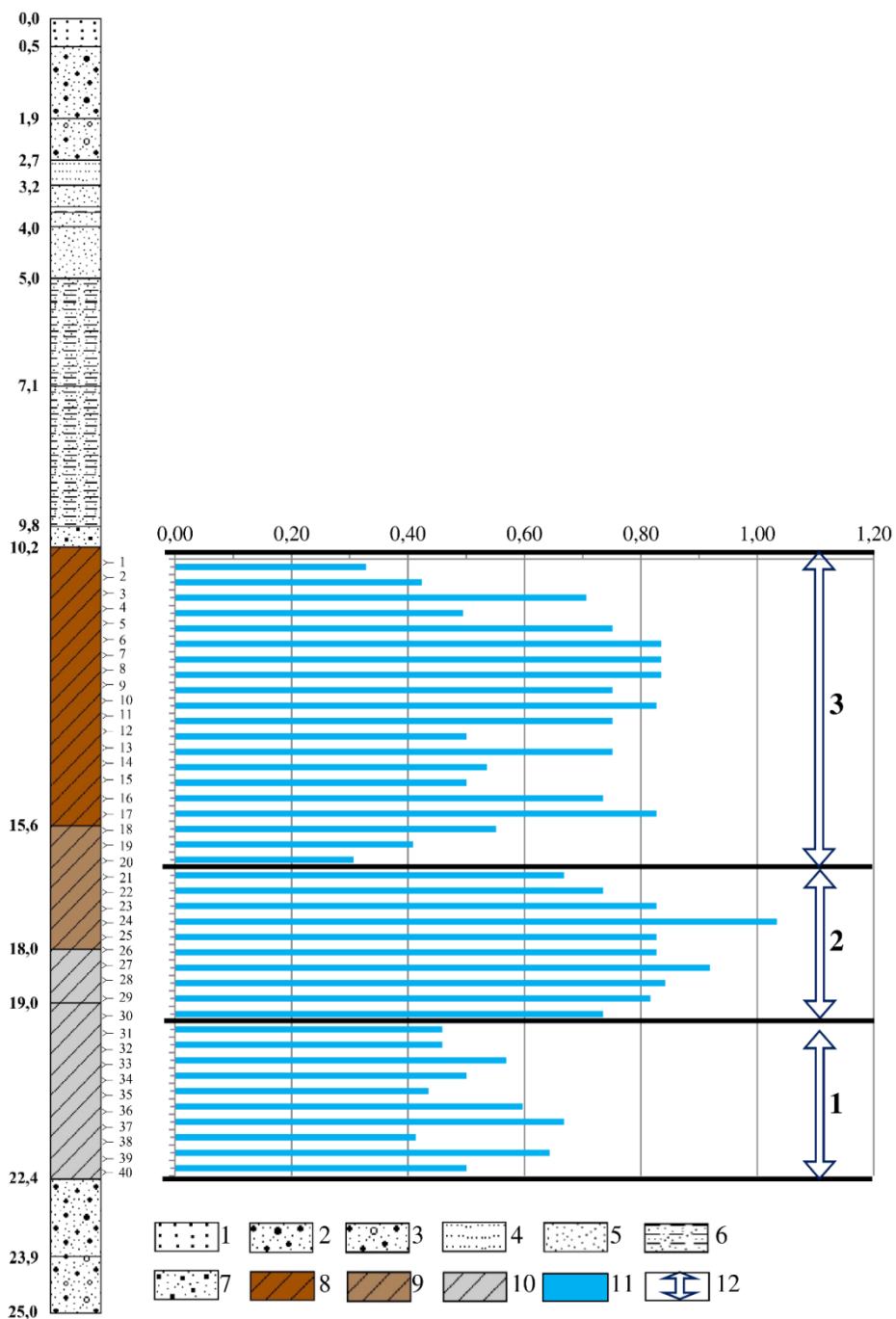


Fig.15. Distribution of glacial deposits in the vertical section of Kusliškès (Gr-1, I) borehole according to the ratio dolomite vs calcite: 1 – coarse-middle-grained sand; 2 – badly sorted sand; 3 – gravely sand; 4 – fine-grained sand; 5 – very fine-grained sand; 6 – aleuritic sand; 7 – various sand; 8 – morainic loam, brown; 9 – morainic loam, greyish brown; 10 – morainic loam, grey; 11 – ratio dolomite vs calcite; 12 – the distinguished different homogeneous till layer. **Note:** In Figs. 15-19, the NN of the borehole mouth is given in parentheses near the borehole number.

According to d:c ratio, using Van der Waerden criterion, three different homogeneous till layers were distinguished in the vertical section of Kusliškės (Gr-1, I) borehole (Fig. 15.).

The percentage of calcite in the 20 cm thick greyish brown till with lenses of fine sand and clay of Strūnaitis (Gr-2, II) borehole ranges from 7.87 to 15.74 %. The percentage of dolomite is slightly lower – from 5.16 to 11.10 %.

According to d:c ratio, using Van der Waerden criterion, five different homogeneous till layers were distinguished in the vertical section of Strūnaitis (Gr-2, II) borehole (Fig. 16.).

The content of calcite in the 1.2 m thick greyish brown sandy loam layer of borehole Vidutinė (Gr-3, III) ranges from 12.36 % to 14.61 %; dolomite from 10.21 to 11.36 %. In the deeper dark brown layer of solid till layer, the content of calcite ranges from 10.12 to 14.77 % and dolomite from 9.09 to 15.66 %.

According to d:c ratio, using Van der Waerden criterion, two different homogeneous till layers were distinguished in the vertical section of Vidutinė (Gr-3, III) borehole (Fig. 17.).

In the lower (first) layer, the ratio between dolomite and calcite varies but little. Glaciolateral evidences are absent.

In the upper (second) layer, the dolomite vs calcite values are lower than in the first layer. It contains the erratics presumably incorporated from the first layer.

The brown morainic loam composing the surface layer of Mineliškės (Gr-4, IV) borehole contains from 5.11 to 14.77 % of calcite and from 4.70 to 11.48 % of dolomite. The layer of brown extremely solid morainic loam bedding at a depth of 5 to 21.3 m contains from 10.99 to 16.86 % of calcite and from 6.06 to 16.34 % of dolomite. In the deeper layer of compact brown sandy loam, calcite accounts for 11.46 to 14.89 % and dolomite for 12.44 to 15.64 % (Fig. 18.).

According to d:c ratio, using Van der Waerden criterion, three different homogeneous till layers were distinguished in the vertical section of Mineliškės (Gr-4, IV) borehole (Fig. 18.).

The variation interval of dolomite vs calcite values in the lower (first) layer is small. Glaciolateral marks are absent.

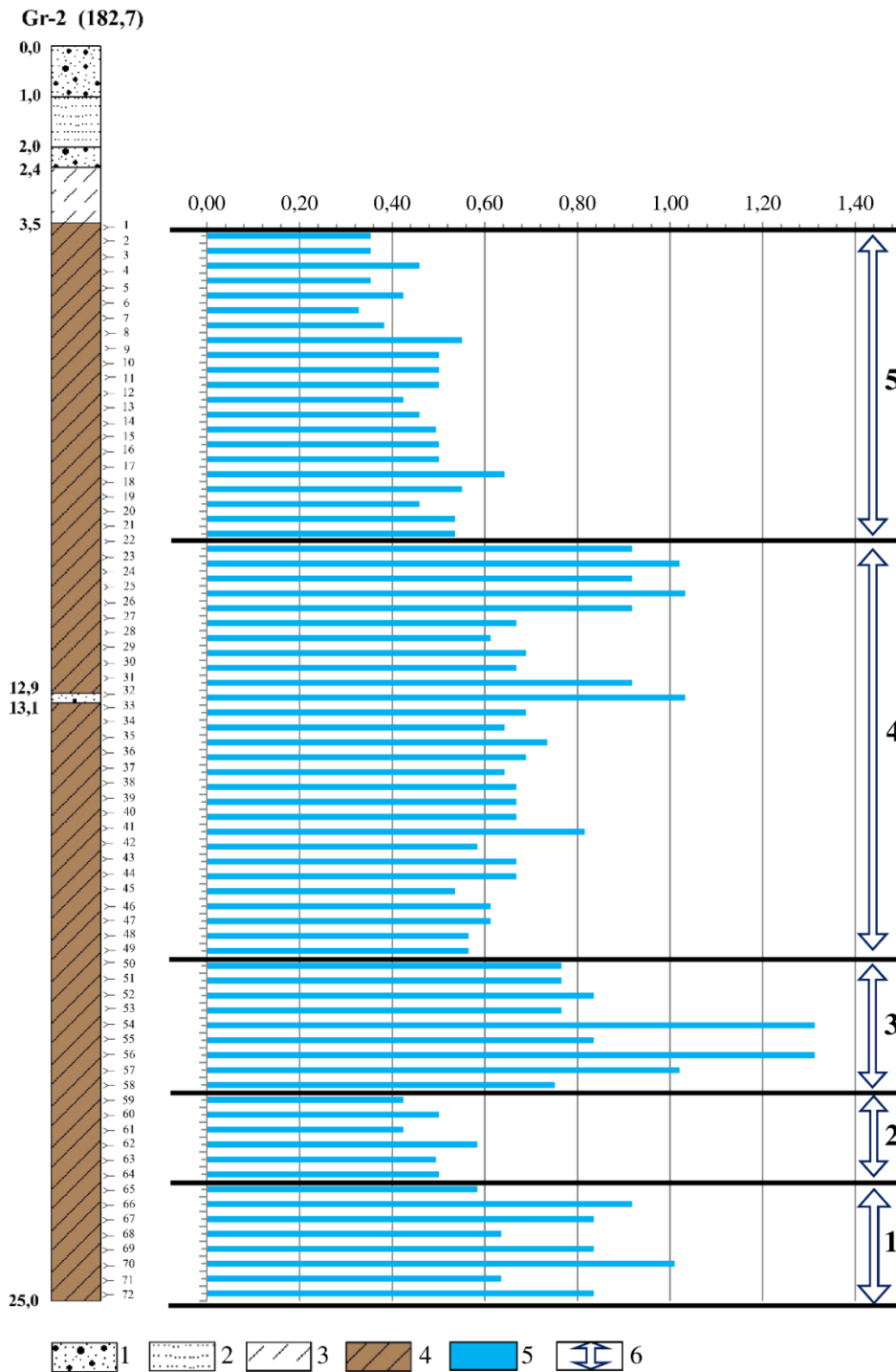


Fig. 16. Distribution of glacial deposits in the vertical section of Strūnaitis (Gr-2, II) borehole according to the ratio dolomite vs calcite: 1 – various sand; 2 – fine-grained sand; 3 – morainic sandy loam; 4 – morainic loam, greyish brown; 5 – ratio dolomite vs calcite; 6 – the distinguished different homogeneous till layer.

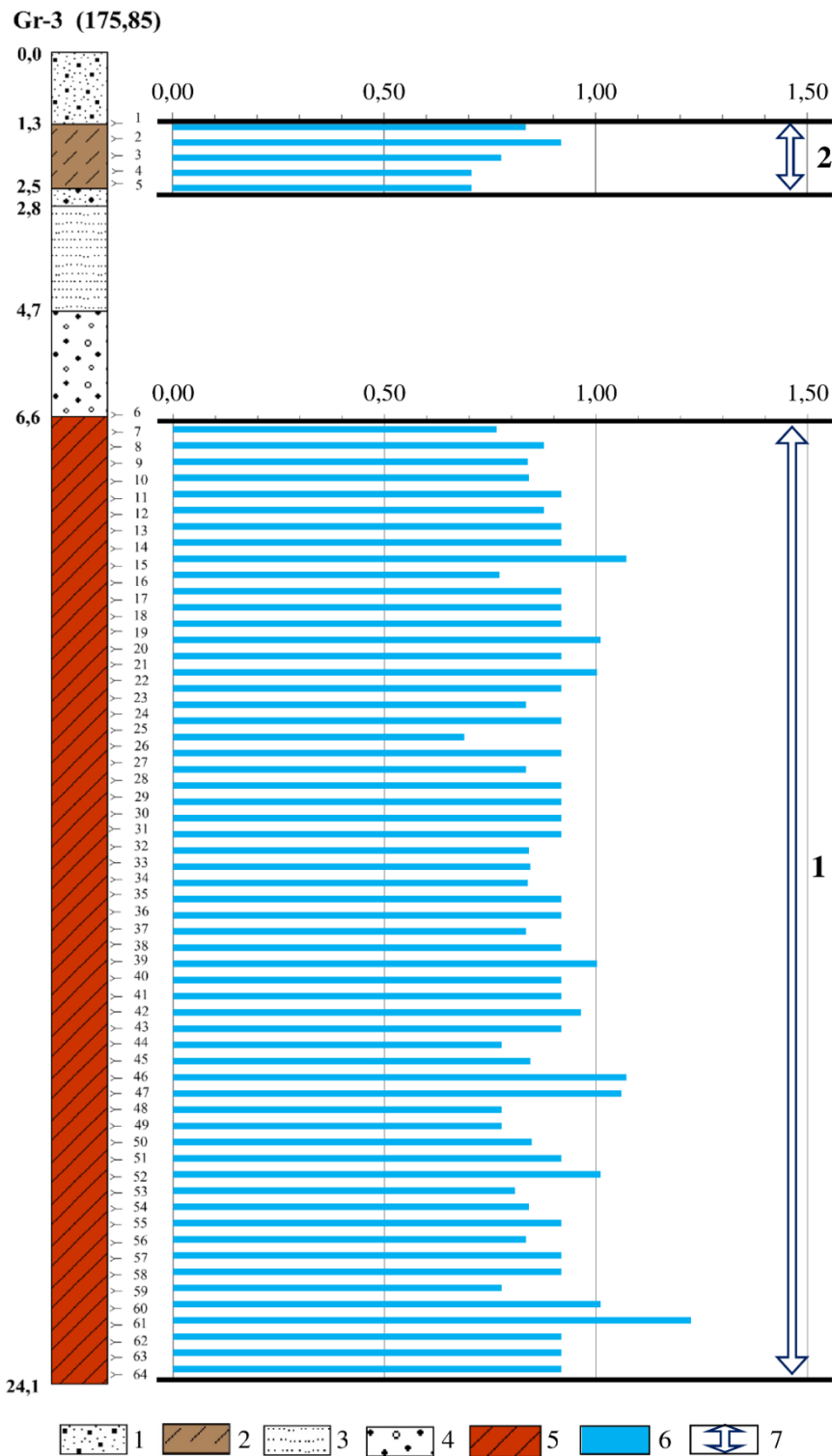


Fig. 17. Distribution of glacial deposits in the vertical section of Vidutinè (Gr-3, III) borehole according to the ratio dolomite vs calcite: 1 – various sand; 2 – morainic loam, greyish brown; 3 – fine-grained sand; 4 – gravel-pebble; 5 – morainic loam, dark brown; 6 – ratio dolomite vs calcite; 7 – the distinguished different homogeneous till layer.

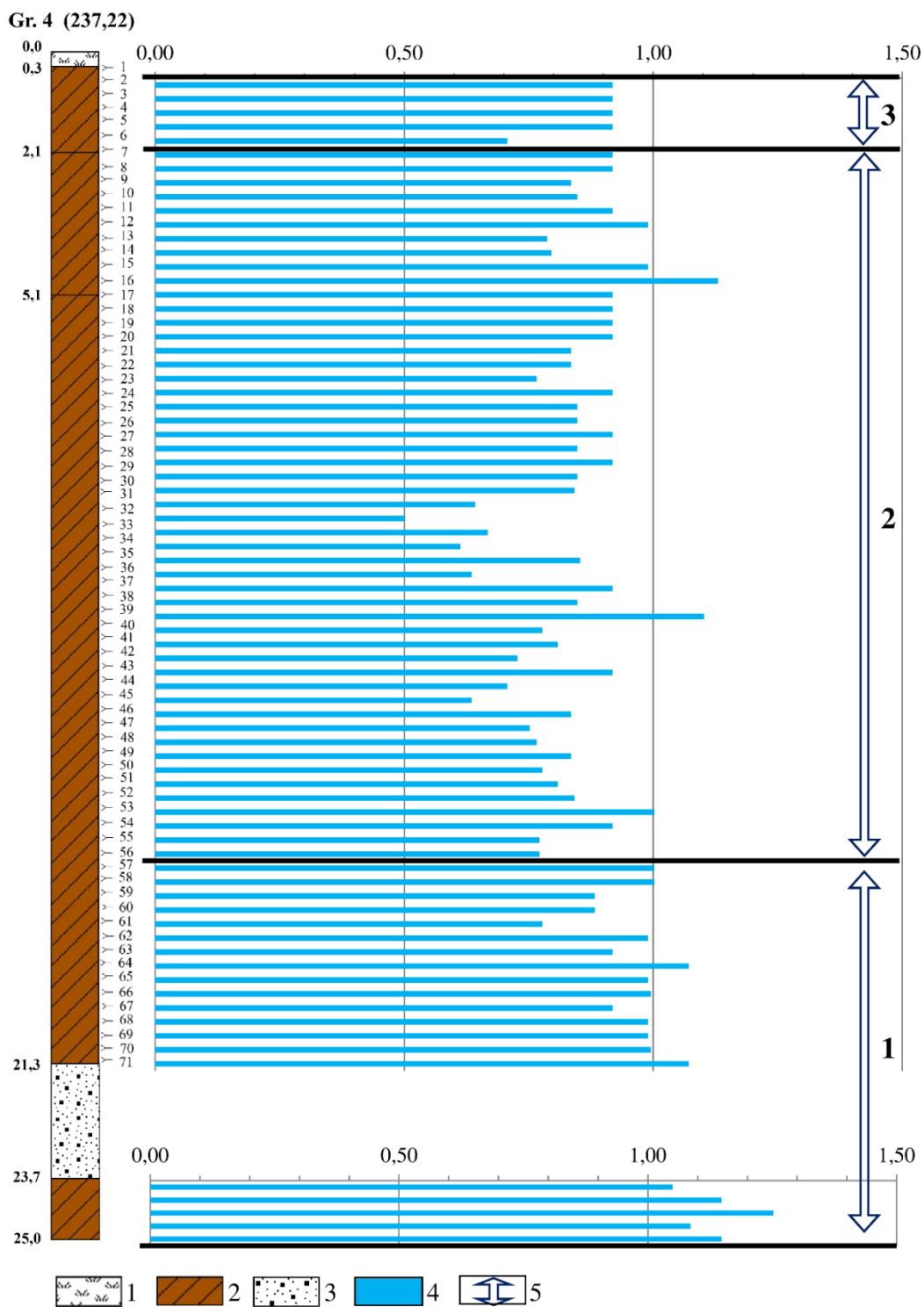


Fig. 18. *Distribution of glacial deposits in the vertical section of Mineliškės (Gr-4, IV) borehole according to the ratio dolomite vs calcite: 1 – soil; 2 – morainic loam, brown; 3 – various sand; 4 – ratio dolomite vs calcite; 5 – the distinguished different homogeneous till layer.*

In the middle (second) layer, the dolomite vs calcite values are close to the values of the lower layer. The lower values of dolomite vs calcite ratio, predetermined by glacioidislocations, lies at the basis of distinguishing the middle layer.

The variation intervals of dolomite vs calcite ratio in the upper (third) layer are small.

Calcite in the brown morainic sandy loam of Papinigiai (Gr-5, V) borehole accounts for about 10–13 % and dolomite for 5–11 %. In the deeper till layers presented by loam and sandy loam, the quantities of dolomite and calcite are almost equal except at a depth interval from 8.4 to 10 m (Fig. 19.).

According to d:c ratio, using Van der Waerden criterion, three different homogeneous till layers were distinguished in the vertical section of Papinigiai (Gr-5, V) borehole (Fig. 19.).

The variation of dolomite vs calcite in the lower (first) layer is inconsiderable.

In the middle (second) layer, the values of dolomite vs calcite ratio are rather variable. The distribution is typical of the layer affected by glacioidislocations. Further collations refer to this layer as a mixture of the upper and lower layers.

In the upper (third) layer, the values dolomite vs calcite are variable, typical for glacial marginal formations.

For verification of hypothesis about the plausibility of dolomite vs calcite as a lithostratigraphic criterion, the investigation of carbonates was conducted including a control analysis of biostratigraphically-subdivided sections: in borehole Snaigupėlė-705 and outcrop of Jonioniai ravine. In the section of Snaigupėlė-705 borehole, the sediments attributed to the Snaigupėlė interglacial are bedded between two till layers: the lower Žemaitija layer and the upper Medininkai layer. The Medininkai till is bedded under the Merkinė interglacial sediments in the outcrop of Jonioniai ravine (Кондратене, 1996; Guobytė, 2004; Guobytė & Satkūnas, 2011, and others). It was determined that the average value of dolomite vs calcite in the till layer under the Merkinė interglacial sediments of the Junioniai outcrop is 1.285. The values in the upper (Medininkai) and lower (Žemaitija) till layers of Snaigupėlė-705 borehole are 0.970 and 0.671 respectively.

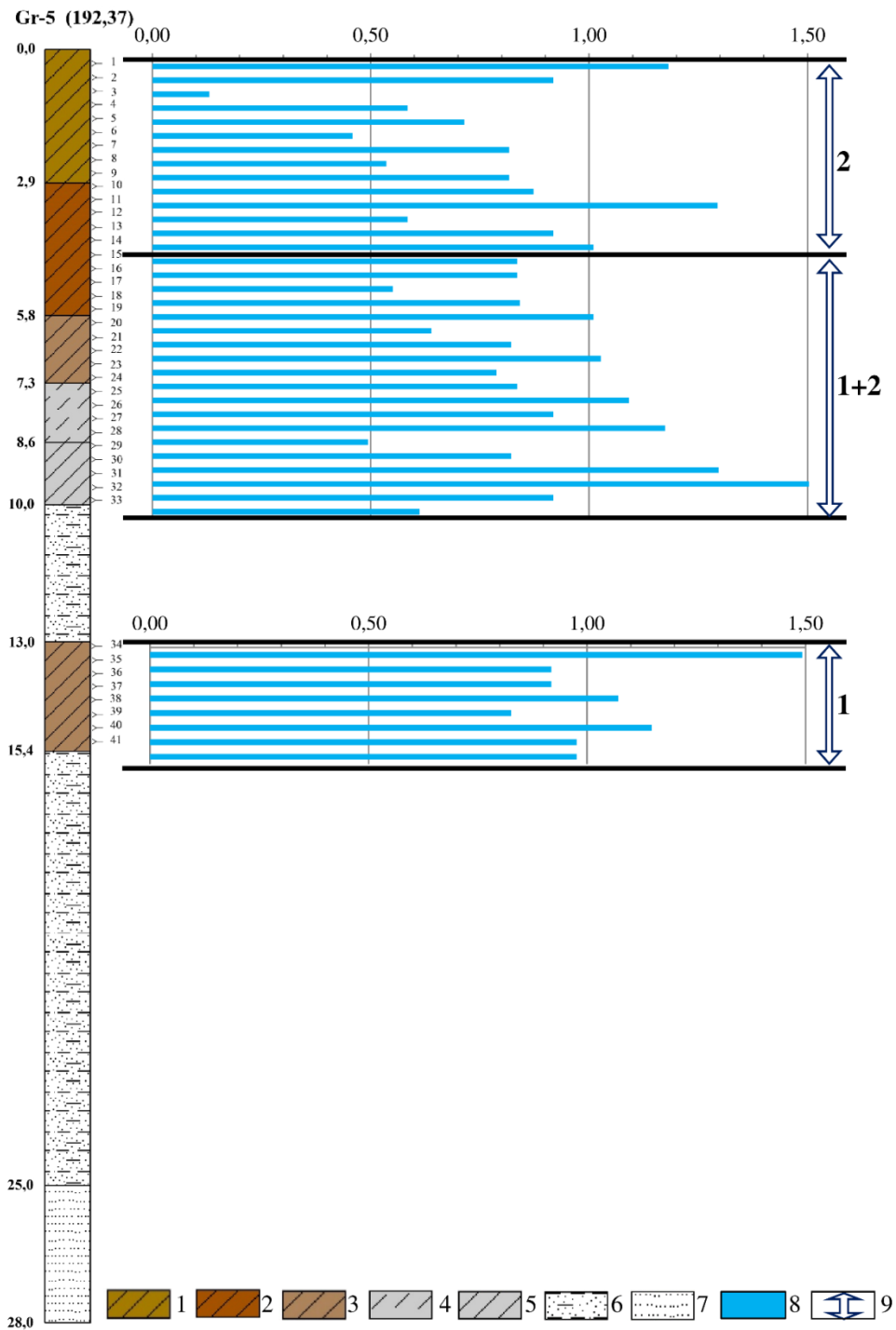


Fig. 19. Distribution of glacial deposits in the vertical section of Papinigliai (Gr-5, V) borehole according to the ratio dolomite vs calcite: 1 – morainic loam, light brown; 2 – morainic loam, brown; 3 – morainic loam, greyish brown; 4 – morainic sandy loam, grey; 5 – morainic loam, grey; 6 – aleuritic sand; 7 – very fine-grained sand; 8 - ratio dolomite vs calcite; 9 – the distinguished different homogeneous till layer.

Along with the samples of till from boreholes the till layers exposed in the outcrops on the slopes of various Lithuanian rivers (Danė, Akmena, Alantas, Ančia, Babrungas, Dubysa, Dūkšta, Gryžuva, Gynėvė, Jura, Kražantė, Kupa, Kvistė, Lazduona, Lėvuo, Minija, Nemunas, Neris, Obelė, Šušvė, Šventoji, Ūla, Varduva, Venta, Vilnelės, Virvytė, and other) were investigated (Fig. 2.).

According to d:c ratio, using Van der Waerden criterion, different homogeneous till layers were distinguished in the vertical sections of investigated outcrops. Below as examples are presented the data obtained from the vertical sections of several outcrops.

According to d:c ratio, using Van der Waerden criterion, two different homogeneous till layers were distinguished in the vertical section of the outcrop at the mouth of the Kvistė River (the left bank of the Varduva River in the environs of Kukiai village).

The Kelmė II outcrop is on the left bank of the Kražantė River in Kelmė. Two different homogeneous till layers were distinguished in this outcrop.

The outcrop Taučiūnai I is in the environs of Taučiūnai village on the left bank of the Obelė River. In its vertical section, two different homogeneous till layers were distinguished.

According to the results of carbonate analysis, one homogeneous till layer was distinguished in the vertical section of Taučiūnai II outcrop in the environs of Taučiūnai village on the right bank of the Obelė River.

The Alantas outcrop is in the environs of Gintarai village on the right bank of the Alantas River. Two different homogeneous layers were distinguished in its vertical sections.

In the vertical section of Skaudvilė outcrop on the left bank of the Ančia River (environs of Skaudvilė borough), two different homogeneous till layers were distinguished.

The Gynėvė outcrop is in the environs of Plikiai village on the left bank of the Gynėvė River. Based on investigation results, one homogeneous till layer was distinguished in its vertical section.

One homogeneous till layer was distinguished in the vertical section of Andriuškoniai outcrop in the environs of Andriuškoniai village on the right bank of the Neris River. The dolomite vs calcite values are variable but their statistical evaluation

using the Van der Waerden criterion shows that they belong to one homogeneous layer. The variations were predetermined by glaciolocations, which are discriminate in the outcrop. The exposed layer has incorporated erratics and smaller clasts of the underbedding till layers. For this reason, according to the quantities of carbonates and dolomite vs calcite values, the outcrop strata of different colours are ascribed to one homogeneous layer.

The Mosteikiai outcrop is in the environs of Mosteikiai village on the left bank of the Gryžuva River. Based on research results, two different homogeneous layers are distinguished in its vertical section.

3.2. Stratigraphic correlation of Pleistocene tills according to mineral composition of carbonates

According to d:c ratio, using Van der Waerden criterion, different homogeneous glacial deposits were distinguished in the vertical sections (Fig. 20.) of all boreholes or outcrops (Fig. 2.)

	A	B	C	D	E	F
1	snaigup	15.052	9.3824	0.6233		
2	snaigup	16.127	9.8762	0.6124		toliau skaičiuoti
3	snaigup	14.45	11.2314	0.7773		2 sluoksnius
4	snaigupvirs	13.3380	14.8050	1.11		
5	snaigupvirs	16.6725	13.2734	0.7961		
6	snaigupvirs	11.2264	11.2501	1.0021		
7						
8						
9						

Fig. 20. Example of the data prepared for calculations, in order to distinguish layers in the vertical section, and conclusions.

The layers distinguished in the investigated boreholes and outcrops according to dolomite vs calcite ratio were subdivided into parts limited from above and from below by the lowest values of the ratio. Homogeneity of the adjacent parts was examined in the vertical direction. Homogeneous parts were joined into one layer and examined repeatedly. In this way, a few (sometimes only one) different homogeneous layers of tills were distinguished.

It should be pointed out that one homogeneous layer includes two or even three parts of till limited by the lowest values of dolomite vs calcite ratio. An assumption is made that these parts of till represent a result of differentiated glacier advance. J.Lavrushin (Лаврушин, 1976) suggested this assumption. During the differentiated glacier advance, sliding surfaces would occur within the glacier and the smaller part of friction-resistant dolomite fragments would be crushed to fine-grained fraction. This is the cause why dolomite vs calcite ratio in these surfaces is lower yet according to correlation index the layers remain homogeneous.

Every layer distinguished in a borehole or outcrop was compared with the layers distinguished in other boreholes or outcrops. In this way, the spatial distribution of homogeneous till layers was established. Comparison was based on the ratio of dolomite and calcite using the Van der Waerden criterion and SAS software.

For calculations using the SAS software, tables of comparative data of layers were preliminary compiled (Fig. 21.).

By calculation using SAS software homogeneous layers are distinguished. Homogeneity is relatively divided into 4 levels: 0 – inhomogeneous (not uniform), 1 – homogeneous (uniform), 2 – distantly homogeneous, 3 – very distantly homogeneous.

A database was compiled in which layers can be grouped according to equivalent parameters (level of uniformity, stratigraphic index, etc.), evaluated, etc. (Fig. 25.).

	GM	GN	GO	GP	GQ	GR	GS	GT	GU	GV	GW	GX	GY	GZ	HA	
1	snaigup	15.0518	9.3824	0.62334	snaigup	15.0518	9.3824	0.6233	snaigup	15.0518	9.3824	0.6233	snaigup	15.0518	9.3824	0.6233
2	snaigup	16.1269	9.8762	0.61241	snaigup	16.1269	9.8762	0.6124	snaigup	16.1269	9.8762	0.6124	snaigup	16.1269	9.8762	0.6124
3	snaigup	14.4495	11.2314	0.77729	snaigup	14.4495	11.2314	0.7773	snaigup	14.4495	11.2314	0.7773	snaigup	14.4495	11.2314	0.7773
4	vizg3sl	4.446	8.6788	1.95205	karolin2sl	15.2189	4.9929	0.3281	karolin1sl	8.696498	8.987274	1.0334	karolin1sl	8.696498	8.987274	1.0334
5	vizg3sl	4.446	9.1893	2.06687	karolin2sl	16.3059	3.9943	0.2450	karolin1sl	8.696498	8.987274	1.0334	karolin1sl	8.696498	9.98586	1.1483
6	vizg3sl	5.0017	9.1893	1.83724	karolin2sl	15.2189	3.9943	0.2625	karolin1sl	8.696498	9.98586	1.1483	karolin1sl	9.78356	9.98586	1.0207
7	vizg3sl	5.0017	10.7208	2.14343												
8	vizg3sl	4.446	9.1893	2.06687												
9	vizg3sl	3.3345	7.1472	2.14341												
10	vizg3sl	1.1115	10.2103	9.18905												
11	vizg3sl	3.4504	7.3957	2.14343												
12	vizg3sl	8.051	8.4522	1.04983												
13	vizg3sl	6.9008	8.4522	1.22481												
14	vizg3sl	6.9008	11.0935	1.60757												
15	vizg3sl	7.4759	8.9805	1.20126												
16	vizg3sl	6.3258	8.9805	1.41966												
17	vizg3sl	6.3258	7.924	1.25265												
18	vizg3sl	6.3258	7.924	1.25265												
19	vizg3sl	6.3258	9.8674	1.55987												
20	vizg3sl	6.9008	8.9805	1.30137												
21	vizg3sl	8.3788	8.7231	1.04109												

Fig. 21. Example of data prepared for calculations in the collation space of till layers.

```

Log - (Untitled)
NOTE: Copyright (c) 2002-2012 by SAS Institute Inc., Cary, NC, USA.
NOTE: SAS (r) Proprietary Software 9.4 (TS1M2)
      Licensed to VILNIUS UNIVERSITY, Site 70137961.
NOTE: This session is executing on the W32_7PRO platform.

NOTE: Updated analytical products:
      SAS/STAT 13.2
      SAS/ETS 13.2
      SAS/OR 13.2
      SAS/IML 13.2
      SAS/OC 13.2

NOTE: Additional host information:
      W32_7PRO WIN 6.1.7601 Service Pack 1 Workstation

NOTE: SAS initialization used:
      real time      3.61 seconds
      cpu time       0.54 seconds

snaigupele_virsut_tarpgrez_plus_tesinys_results.sas
PROC IMPORT DATAFILE="C:\Users\Eugenija\Documents\Eugenija SAS Files\Paketa"
  DBMS=EXCEL REPLACE;
  GETNAMES=NO;
RUN;

PROC NPAR1WAY VW DATA=Duomenys;
  CLASS F1;
  VAR F4;
RUN;

PROC NPAR1WAY VW DATA=Duomenys;
  CLASS F6;
  VAR F9;
RUN;

```

Fig.22. SAS prepared for calculation in the collation space of till layer distinguished in the vertical section.

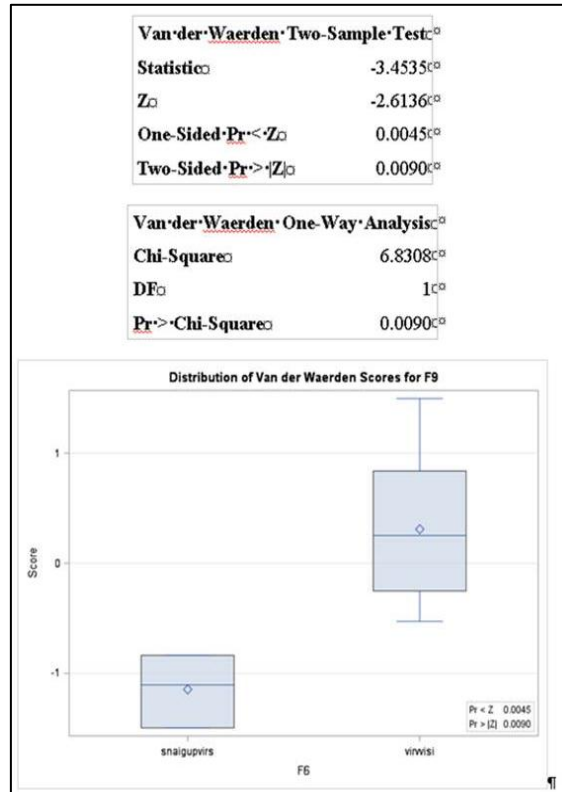


Fig. 23. Example of results obtained using SAS and showing that the layers are different.

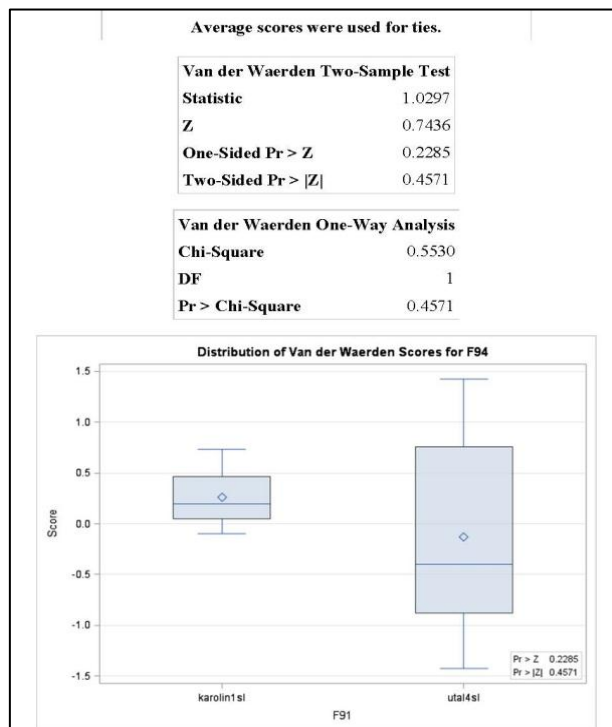


Fig. 24. Example of results obtained using SAS and showing that the layers are similar.

The database is composed of over 100 vertical carbonate analysis results obtained from vertical sections according to homogeneity level. For this purpose 8.6 thousand collations were performed using Van der Waerden criterion. A matrix of homogeneity of layers was worked out (Fig. 26).

Collation of different till layers in the vertical sections is based on the homogeneity matrix of layers worked out using Van der Waerden criterion (Fig. 26.). A correlation scheme of till layers in shallow boreholes is given as an example of effectiveness of this stratigraphic correlation method. The boreholes were drilled in the Švenčionys Highland distinguished for especially complex composition of marginal morain with widespread glacioidislocations, i.e. occurrence of reworked older layers of till (erratics) in the younger ones (Figs 27– 28.).

The mentioned correlation was determined based on the matrix fragment given in Fig. 26 encompassing the evaluation of homogeneity of layers after expertise procedure (Table 3.2.1).

	A	D	G	H	I	J	K
1	Sluoksnis 1	Sluoksnis 2	Lyginami sluoksniai	Panašumas (0,1,2,3)	Ekspertinis vertinim		53
135	Snaig705gr: 2	Jonionys: 1	Snaig705gr: 2 - Jonionys: 1	1	1		
137	Snaig705gr: 2	Kaps4sl: 2	Snaig705gr: 2 - Kaps4sl: 2	1	1		
143	Snaig705gr: 2	Kaps6sl: 4	Snaig705gr: 2 - Kaps6sl: 4	1	1		
146	Snaig705gr: 2	Karmazat: 1	Snaig705gr: 2 - Karmazat: 1	1	1		
148	Snaig705gr: 2	Šve1gr: 2	Snaig705gr: 2 - Šve1gr: 2	1	1		
150	Snaig705gr: 2	Šve2gr: 1	Snaig705gr: 2 - Šve2gr: 1	1	1		
152	Snaig705gr: 2	Šve2gr: 3	Snaig705gr: 2 - Šve2gr: 3	1	1		
155	Snaig705gr: 2	Šve3gr: 1	Snaig705gr: 2 - Šve3gr: 1	1	1		
156	Snaig705gr: 2	Šve3gr: 2	Snaig705gr: 2 - Šve3gr: 2	1	1		
157	Snaig705gr: 2	Šve4gr: 1	Snaig705gr: 2 - Šve4gr: 1	1	1		
158	Snaig705gr: 2	Šve4gr: 2	Snaig705gr: 2 - Šve4gr: 2	1	1		
159	Snaig705gr: 2	Šve4gr: 3	Snaig705gr: 2 - Šve4gr: 3	1	1		
160	Snaig705gr: 2	Šve5gr: 1	Snaig705gr: 2 - Šve5gr: 1	1	1		
161	Snaig705gr: 2	Šve5gr: 2	Snaig705gr: 2 - Šve5gr: 2	1	1		
165	Snaig705gr: 2	Mick7sgr: 4	Snaig705gr: 2 - Mick7sgr: 4	1	1		
183	Snaig705gr: 2	Utal440gr: 4	Snaig705gr: 2 - Utal440gr: 4	1	1		
185	Snaig705gr: 2	Karolingrat: 1	Snaig705gr: 2 - Karolingrat: 1	1	1		
189	Snaig705gr: 2	Gandingat: 1	Snaig705gr: 2 - Gandingat: 1	2	1		
191	Snaig705gr: 2	Skaudvat: 1	Snaig705gr: 2 - Skaudvat: 1	1	1		
198	Snaig705gr: 2	Vetygat: 1	Snaig705gr: 2 - Vetygat: 1	1	1		
201	Snaig705gr: 2	Norkaičat: 2	Snaig705gr: 2 - Norkaičat: 2	1	1		
202	Snaig705gr: 2	Norkaičat: 3	Snaig705gr: 2 - Norkaičat: 3	2	1		
204	Snaig705gr: 2	Pakastuvgr: 1	Snaig705gr: 2 - Pakastuvgr: 1	3	1		
205	Snaig705gr: 2	Pakastuvgr: 2	Snaig705gr: 2 - Pakastuvgr: 2	1	1		
206	Snaig705gr: 2	Pakastuvgr: 3	Snaig705gr: 2 - Pakastuvgr: 3	1	1		
211	Snaig705gr: 2	Svirkat2sl: 1	Snaig705gr: 2 - Svirkat2sl: 1	3	1		
212	Snaig705gr: 2	Svirkat2sl: 2	Snaig705gr: 2 - Svirkat2sl: 2	1	1		
213	Snaig705gr: 2	Svirkat3sl: 1	Snaig705gr: 2 - Svirkat3sl: 1	1	1		

Fig. 25. The database provides a possibility to group layers according to the chosen equivalent parameters. The given example shows collation of homogeneous layers; homogeneity level 1 (after expert evaluation) was chosen as the equivalent parameter.

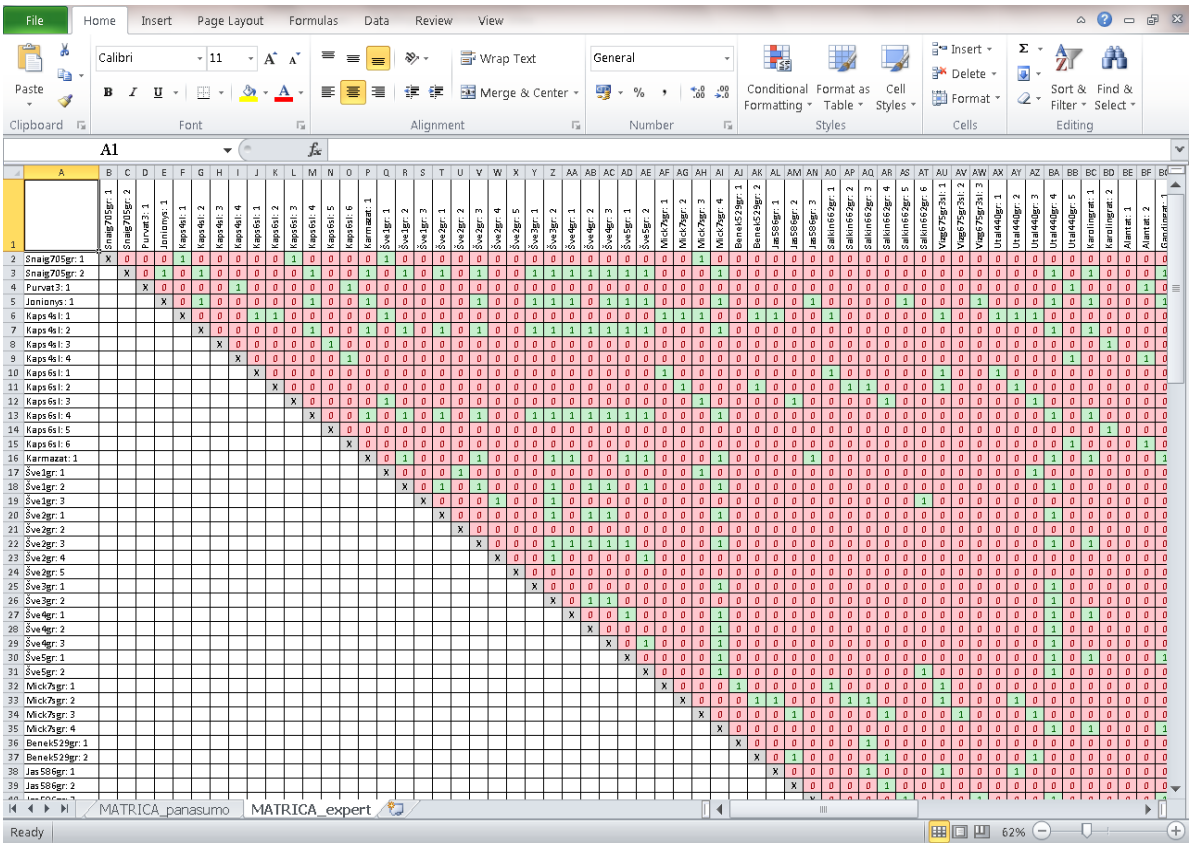


Fig.26. Example of a fragment of homogeneity matrix worked out using SAS-calculated Van der Waerden criterion. Green colour and figure 1 mark horizontal homogeneous layers; red colour and figure 0 mark inhomogeneous layers.

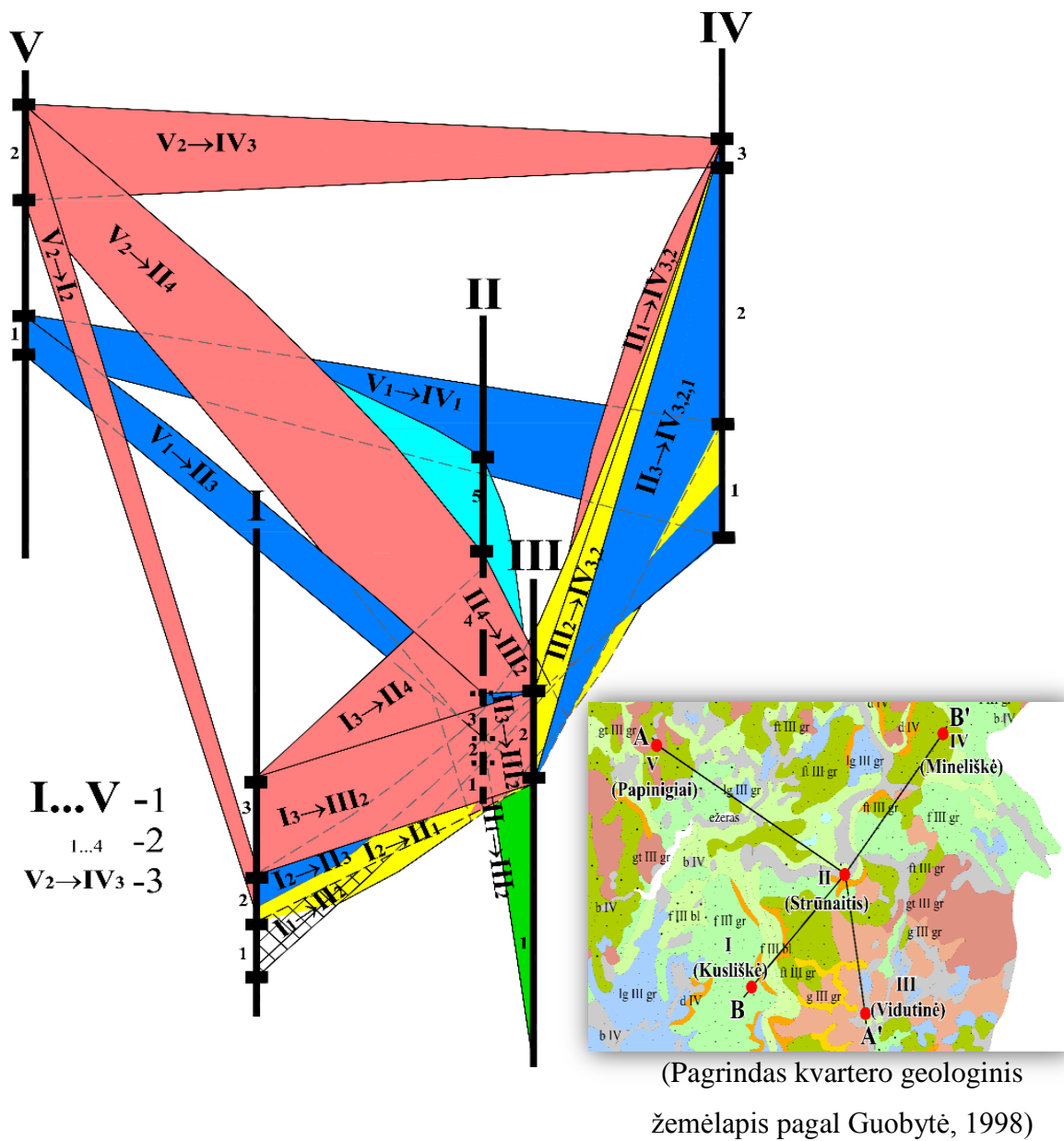


Fig. 27. Planar distribution of shallow cartographic boreholes in the Švenčionys Highland and block diagram of correlation links of homogenous layers.

1 – borehole numbers; 2 – numbers of distinguished homogeneous layers;
 3 – relationships of the distinguished layers.

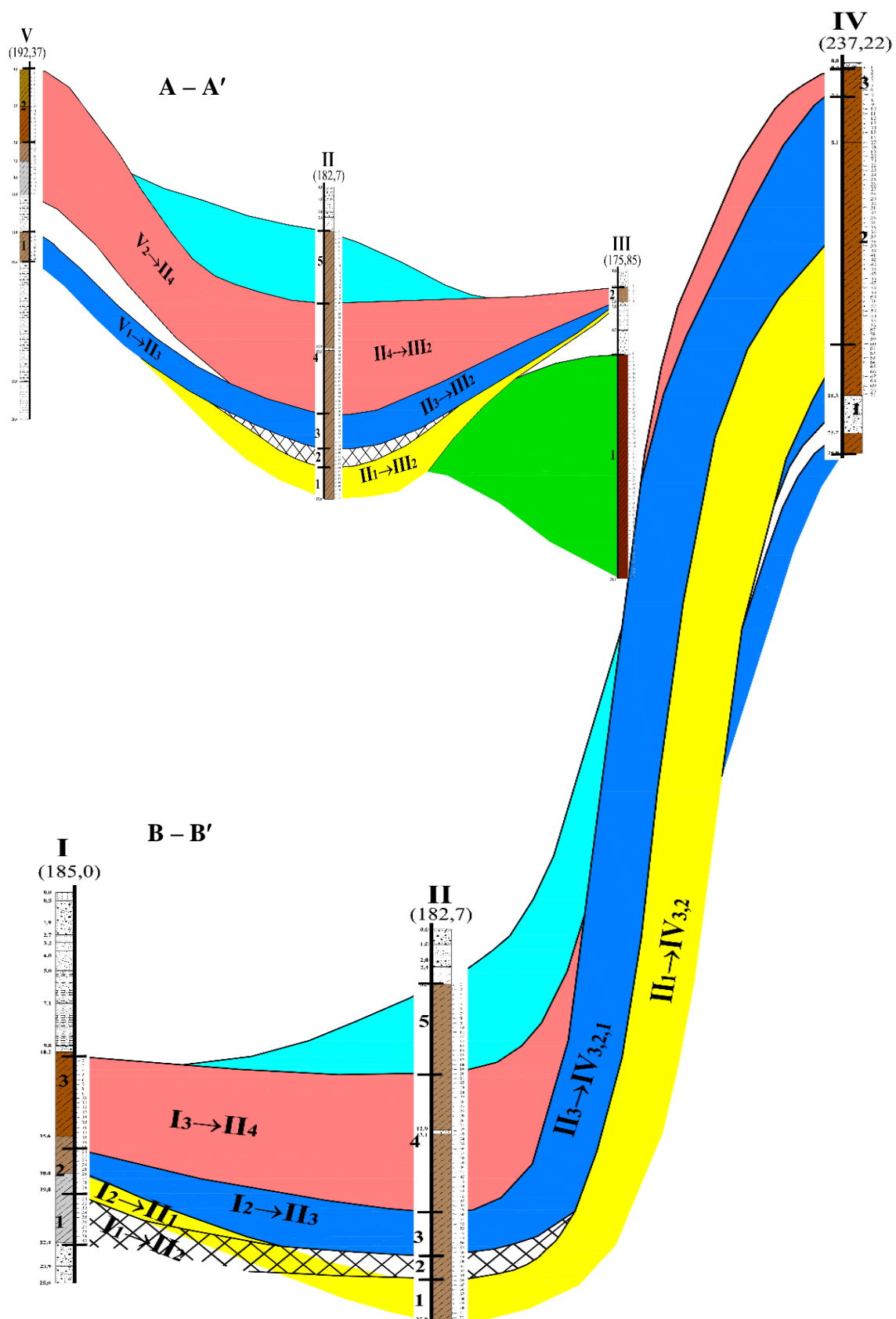


Fig. 28. Correlation scheme of inhomogeneous tills layers in sections A-A' and B-B'.

Development of stratigraphic correlation scheme of tills for further individual geological sections may chance “criss-cross” correlation of layers what is impossible in natural environment. This situation, especially in the zone of glacial marginal formations, is explainable by correlation of the same layers, which in one borehole are bedding *in situ* whereas in the other borehole it is bedding as a till erratic (not *in situ*) incorporated in the layer of younger till. For example, correlation layers I₁ – II₂ and I₂ – II₁ layers (Fig. 27.) in the same scheme is impossible: one correlation link should be eliminated and interpreted as result of glaciotectonic dislocation.

It is a common case when during stratigraphic correlation till layers in one borehole are distinguished as inhomogeneous but in the final version they are ascribed to the layer of the same glacial advance (stage, substage).

The stratigraphic subdivision of spatially correlated till layers is determined according to the established index d:c for these layers. This index also may be helpful in determining the stratigraphic subdivision of erratics incorporated in younger tills (*ex situ*) (Table 3.2.2).

The aim of further investigation was to compare all till layers distinguished according to d:c ratio and to subdivide them into stratigraphic units. In the future, the layers distinguished in new investigated vertical sections also could be stratigraphically subdivided. For this purpose, every newly distinguished layer could be collated with all investigated layers using SAS and by Van der Waerden criterion homogeneous layers could be determined vertically and horizontally. The next step would include search for homogeneous layers and determination of presumptive stratigraphic position of investigated layer.

The obtained data showed that according to d:c ratio the investigated vertical sections include up to 6 heterochronous till layers.

In heterochronous tills the quantities and ratio of dolomite and calcite are rather variable. In three lower (the deepest ones in the vertical sections) till layers are predominated by calcite; the ratio d:c ranges on the average within intervals 0.290–0.450; 0.470–0.500; 0.510–0.810 respectively.

Table 3.2.2 Stratigraphic interpretation of till layers in the boreholes of the Švenčionių Highland according to their mutual correlation, spatial bedding and estimated dolomite vs calcite ratio (d:c)

The layer assignment to the stratigraphic unit	No of layer in the borehole	Occurrence conditions	The average d:c	Remarks
Upper Nemunas Baltija (bl) vs Grūda (gr) Subformation	II ₅	<i>in situ</i>	0,45-0,5	
Upper Nemunas Grūda (gr) Subformation	V ₂	<i>ex situ</i>	0,85-1,1	Layer with erratic of older till (md)
	III ₂	<i>ex situ</i>	0,75	Layer enriched by lamps of till (md)
	II ₄	<i>in situ</i>	0,7	
	I ₃	<i>in situ</i>	0,6	
Medininkai (md) Formation (marginal moraine)	V ₁	<i>in situ</i>	0,95-1,1	
	IV ₃	<i>ex situ</i>	0,82	Possible erratic of older till (žm)
	IV ₂	<i>ex situ</i>	0,89	—, —
	IV ₁	<i>in situ</i>	1,15	
	II ₃	<i>in situ</i>	0,8-1,0-1,2	
	II ₂	<i>ex situ</i>	0,5	Erratic of older till (dn?)
	II ₁	<i>ex situ</i>	0,6-0,85	Erratic of older till (žm)
	I ₂	<i>ex situ</i>	0,85	—, —
	I ₁	<i>ex situ</i>	0,5	Erratic of older till (dn?)
Žemaitija (žm) Formation vs Dainava (dn) Formation	III ₁	<i>in situ</i> (?)	0,53	Interpretation of layer bedding, without data about the deeper layers, is problematic

Dolomite is clearly dominant in the fourth till layer. The ratio d:c ranges within 0.920–1.0 or exceeds 1. The ratio of dolomite and calcite in the fifth layer is approximately equal. It is close to 1 and ranges within the interval 0.820–0.910. The sixth layer is slightly predominated by calcite. The ratio d:c ranges within the interval 0.600–0.810.

Thus, the distinguished lithostratigraphic criterion – ratio dolomite *vs* calcite – may serve as a correlation index. The fourth layer (counting upwards from the deepest ones), where dolomite is dominant and the ratio d:c is close to or exceeds 1.0, could serve as a marker horizon.

The author of the present study referred to biostratigraphic classification of the Lithuanian Quaternary thickness developed by other researchers (Кондратене, 1993; 1996; ir kt.). The history of stratigraphic investigations is generalized in the articles by R. Guobytė (2002; 2004), R. Guobytė and J. Satkūnas (2011) and others.

After the ratification of the lower boundary of the Quaternary (Gibbard & Head, 2010), Lithuania still did not adopt the new general scheme of stratigraphic classification of the Quaternary. The newest classification was confirmed by the LGS in 2005 and the newest comment was published in 2007 in *Journal of Geology* published by the Lithuanian Geological Society (“*Geologijos akiračiai*”) (Satkūnas et al., 2007). Researchers propose different versions (Satkūnas et al., 1997; 1998; 2003; 2009; Kondratienė, 2011, and others). O. Kondratienė suggests biostratigraphic schemes (Кондратене, 1993; 1996). V. Šeirienė with co-authors (Šeirienė et al., 2015) introduces a chronostratigraphic correlation scheme of Pleistocene for Belarus and Lithuania comparing it with the West European one, standard scale and marine oxygen isotope studies (MIS).

Below follow equivalents of different values of lithostratigraphic criterion (d:c ratio) for stratigraphic units in simplified Lithuanian Quaternary Stratigraphic Scheme accepted for geological mapping in the Lithuanian Geological Survey (Lietuvos..., 2009).

Table 3.2.3. Stratigraphic assignment of till layer according to value of dolomite vs calcite ratio (d:c)

The layer assignment to the stratigraphic unit	Value of d:k ratio (from –to)
Upper Nemunas Baltija (bl) Subformation	0,600 - 0,810
Upper Nemunas Grūda (gr) Subformation	0,820 - 0,910
Medininkai (md) Formation	0,920 - ≥ 1
Žemaitija (žm) Formation	0,510 - 0,810
Dainava (dn) Formation	0,470 - 0,500
Dzūkijos (dz) Formation	0,290 - 0,450

The values of d:c “from–to” given in the scheme for heterochronous till layers will allow applying this index for lithostratigraphic subdivision of glacial deposits of the Lithuanian Quaternary and will contribute to the full-scale knowledge of the Quaternary thickness formation.

In order to accurately identify and correlate till layers according to this lithostratigraphic criterion it is necessary to conduct calculations of Van der Waerden criterion using SAS and to compare the obtained data with the database and matrix.

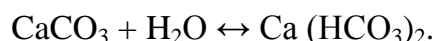
Based on the obtained data the author maintains that the quantities and ratio of dolomite and calcite (d:c) can serve as correlation index. The Medininkai till, in which dolomite is dominant and the ratio d:c is close, equal or exceeds 1.0, can be taken as a marker horizon.

3.3. Carbonates of non-glacial sediments

Sediments and deposits of a few interglacials occur in the territory of Lithuania. These lithological chronicles contain information about past sedimentation and climate conditions. In the present study, specific features of carbonate sedimentation in

heterochronous Pleistocene interglacials and Holocene were investigated for their informativeness as indicators of palaeoclimate conditions.

Carbonates in different lithological varieties of interglacial lake sediments occur as impurities. The purely carbonate-composed interglacial sediments are infrequent. Monocarbonate CaCO_3 , which is an almost insoluble compound (solubility 0.001 g in 100 g of water), under the conditions of excess CO_2 turns to highly soluble bicarbonate compound $\text{Ca}(\text{HCO}_3)_2$. The natural waters are characterized by resilient balance:



Elimination of excess CO_2 disturbs the balance shifting towards formation of water insoluble monocarbonates (Pansu, Gautheyrou 2006). Formation of especially thin dispersed carbonates in the interglacial lacustrine sediments can be accounted for by the inflow of terrigenous sediments whose fine particles act as agents of crystallization of carbonate precipitation from the aqueous solution. Depending on the composition of the agent of crystallization, either CaCO_3 or $\text{CaMg}(\text{CO}_3)_2$ precipitate. The precipitated carbonates consolidate and are covered by clayey membrane and buried.

The content of carbonates varies depending on the factors influencing the content of CO_2 in the water. Warming of the water, organism and plant activity or currents and waves, eliminating CO_2 and forming potential crystallization centres, are among the main factors causing reduction of the content of CO_2 and carbonate precipitation.

The interglacial climate oscillations played the key role in formation of extremely thin dispersed carbonates. Climate oscillations affected water temperature, vegetation and organisms who, in their turn, affected content of CO_2 in lake water and the latter controlled formation of chemogenic and biochemogenic carbonates in clastogenic sediments.

The applied research methods allow determining not only calcite but dolomite as well. For this reason, the determined bulk content of carbonates exceeds the one determined by other methods (Kozlovsky's, titration, etc.). This aspect is important in using carbonate content for palaeogeographical reconstructions; the identified quantities of dolomite show higher or lower input of terrigenous material and allow determining with greater accuracy the climate conditions during sedimentation (Рудницкайте, 1984).

Investigation of heterochronous Lithuanian Pleistocene interglacial and Holocene sediments showed that carbonate quantities in them are variable both in monochronous and heterochronous vertical sections.

Non-glacial sediments were investigated in sections of 12 boreholes and 30 outcrops.

A few examples of obtained data are given below.

Butėnai outcrop. The section of interglacial lacustrine sediments in the South Lithuanian Anykščiai District on the left bank of the Šventoji River, near Janonys village, is a stratotype of the Butėnai interglacial. Publicising the first investigation data about this outcrop, O. Kondratienė (1962) points out that A. Kondratas discovered it in 1953. Since then, many researchers have investigated the sediments of the outcrop, which are important for stratigraphical subdivision of the Lithuanian Quaternary. O. Kondratienė generalized the conducted investigations in a monograph (1996). During a large-scale geological mapping in 1984–1986, sediments of this time were detected also in boreholes drilled in Trumpaliai, Šiekštys, Sudeikiai, Gaigalai and other localities. The obtained results allowed determining the distribution area of interglacial palaeolakes. According to O. Kondratienė (1996), the stratigraphic location of the Butėnai interglacial causes no uncertainties neither in subdivision of the Lithuanian Quaternary nor in comparison with stratigraphic subdivisions of other countries.

In the present study, carbonates of exposed sediments of Butėnai outcrop were investigated. The distribution of carbonates in the vertical section was examined in 29 samples from a 2 m thick layer. Comparison with the data of pollen and diatomic analyses is hampered by the fact that results were obtained from different samples. The carbonate composition of this section is distinguished for prevalence of dolomite against calcite almost across the section (Fig. 29.). According to carbonate data, two time spans can be distinguished in the lower part of the section: cold time span (interval 2.6–2.16) and rather warm time span (interval 2.16–0.76 m) with cooling at 1.19 m. The cooling span divides the interval into two parts: the lower part, which represents longer and warmer period, and the upper part, which represent shorter cooling period after which climate never warmed up to the previous level.

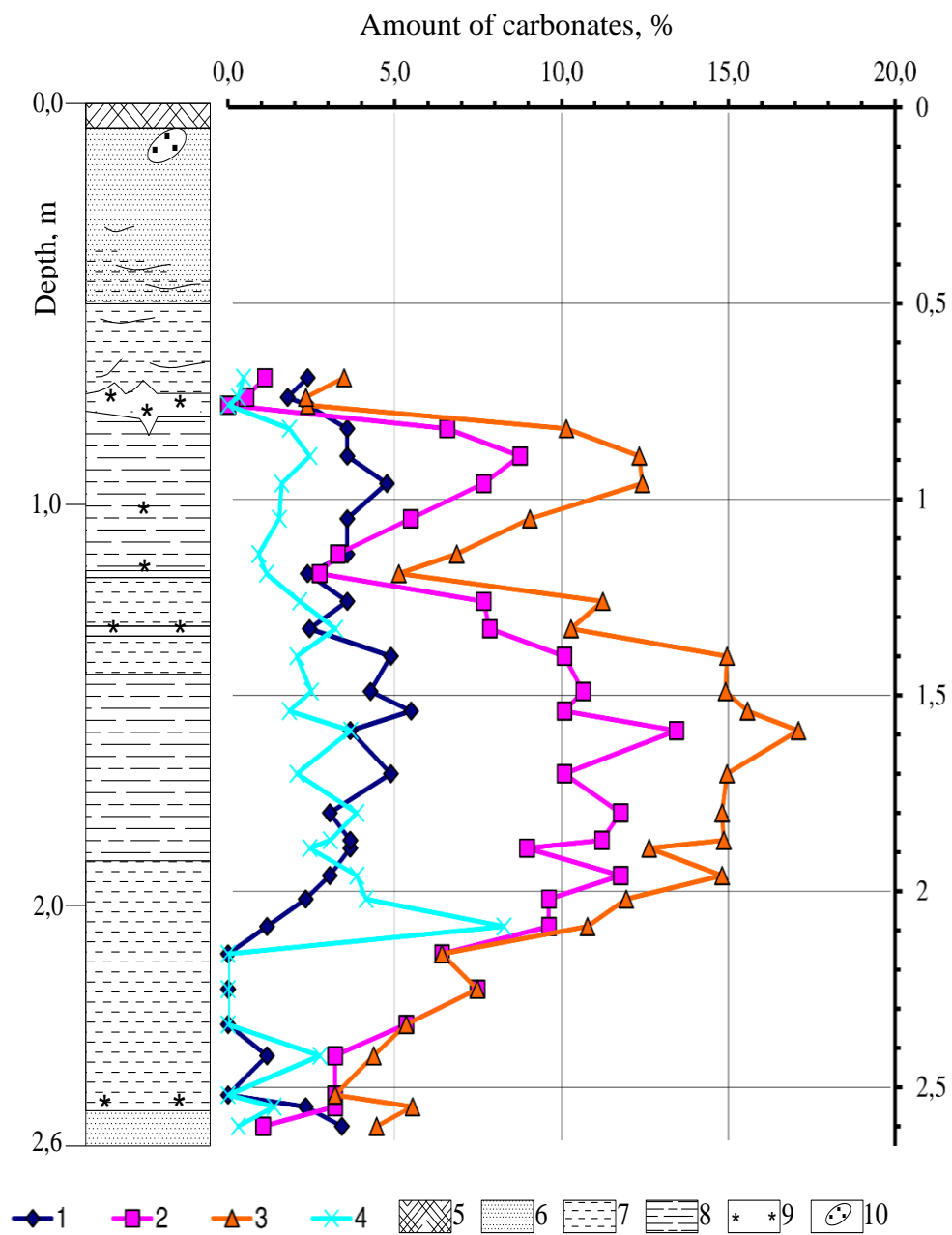


Fig. 29. Carbonates in the sediments of Butènai outcrop: 1 – calcite, %; 2 – dolomite, %; 3 – bulk content of carbonates, %; 4 – dolomite vs calcite; 5 – soil; 6 – fine-grained sand; 7 – aleurite; 8 – aleurite with clay interlayer; 9 – limonization; 10 – weathered boulder.

Carbonate content in the sediments within the interval 2.6–2.16 m evidences cold climate conditions occurring at the beginning or end of glaciations. More intensive dolomite deposition implies also more intensive transportation of terrigenous material.

In the interval 2.16–1.19 m, dolomite content exceeds the content of calcite. Both curves bear pulsating character reflecting responses to seasonal changes. The depth 1.59 m marks the optimum of the time span corresponding to the interglacial.

Within the interval 1.19–0.76 m, the curves (without noticeable pulsations) reach their maximum at 0.96–0.89 m. This warming rather resembles an interstadial followed by warming what is reflected in carbonate content curves gradually descending to minimal values.

The interval 2.16–0.76 in general can be evaluated as an interglacial with two optimums and cooling between them.

The obtained data are in conformity with pollen and diatomic data. The slightly lower carbonate values than is typical of interglacials were predetermined by that sedimentation took place in a rather deep eutrophic lake (Шейрене, 1993).

Borehole Snaigupėlė-705. In her investigation of the differences between Snaigupėlė interglacial plant evolution and plant evolution during Butėnai and Merkinė interglacials O. Kondratienė distinguishes a discrete interglacial pointing out that its most complete section is represented by Snaigupėlė-705 borehole. The stratigraphic location of Snaigupėlė interglacial remains problematic. When in 2005, the sediments from this borehole were dated using OSL, TL, ESR and Th/U methods (Gaigalas, Arslanov et al., 2005; Gaigalas, Fedorowicz et al., 2005) and the obtained results confirmed the discreteness of the interglacial it seemed that the problem was resolved. Yet in 2015, having analysed the research history of Snaigupėlė and conducted palaeomagnetic investigations, Baltrūnas with co-authors (Baltrūnas et al., 2015) maintained that the palaeomagnetic inversion discovered in the sediments of Snaigupėlė outcrop is related with the Blake even in the Merkinė (Eemian) interglacial.

The sediments of Snaigupėlė interglacial investigated in Snaigupėlė-705 borehole separate tills of two discrete glaciations. The section was investigated from bottom upwards, i.e. from the oldest to the youngest sediments. O. Kondratienė has distinguished 9 pollen zones. The first of them is related to the Late Žemaitija glacial and the ninth to

the first half of the Medininkai glacial. The distribution of carbonates confirms this interpretation. In both zones, the content of dolomite exceeds the content of calcite. This evidences intensive denudation, i.e. intensive transport of terrigenous material into the basin.

The content of carbonates in the sediments at a depth of 32.9–35.8 m is variable. The content of calcite tends to decrease whereas pulsatile increase is characteristic of dolomite content, which considerably exceeds the content of calcite.

At a depth of 31.0–32.9 m, the content of dolomite decreases whereas the content of calcite remains low.

At a depth interval from 31.0 to 27.0 m, the content of dolomite and calcite increases. The rates of calcite increase are higher and within the interval 26–27 m the content of calcite exceeds the content of dolomite.

The increase of the bulk content of carbonates to 30–31 % is in correlation with the interglacial climate optimum. The quantity of calcite is higher than that dolomite. The bedding depth of the sediments is 21.5–26.0 m. Oaks with nut-tree undergrowth, oaks with hornbeam and hornbeam forests grew during the Snaigupėlė interglacial. According to O. Kondratienė, the Snaigupėlė interglacial embraces the upper part of the fourth pollen zone, fifth pollen zone and the lower part of the sixth pollen zone (Кондратене, 1996).

It is assumed that the possibly karst lake was very deep. This assumption is based on the species composition of diatomic algae (Хурсевич, 1984) and presence of hydrotroilite in the lower part of the section, which in recent lakes is deposited at a depth exceeding 20–25 m (Garunkštis, 1958; Гарункштис, 1975). O. Kondratienė (Кондратене, 1996) maintains that in the initial stage of existence the lake depth could have been over 30 m.

Meilės Sala outcrop. The outcrop is in Druskininkai on the left bank of the Nemunas River in front of Meilės Sala. P. Vaitiekūnas (Vaitiekūnas, 1969) ascribed the sediments of the upper part to the Merkinė interglacial. The distribution of carbonates in the sediments is uneven. The sections were investigated from the bottom upwards, i.e. from the oldest to the youngest sediments (Fig. 30.).

The carbonate curves in the interval 3.79–3.73 m reflect rather warm climate with moderate summers and winters. The depth 3.75 m marks climate warming.

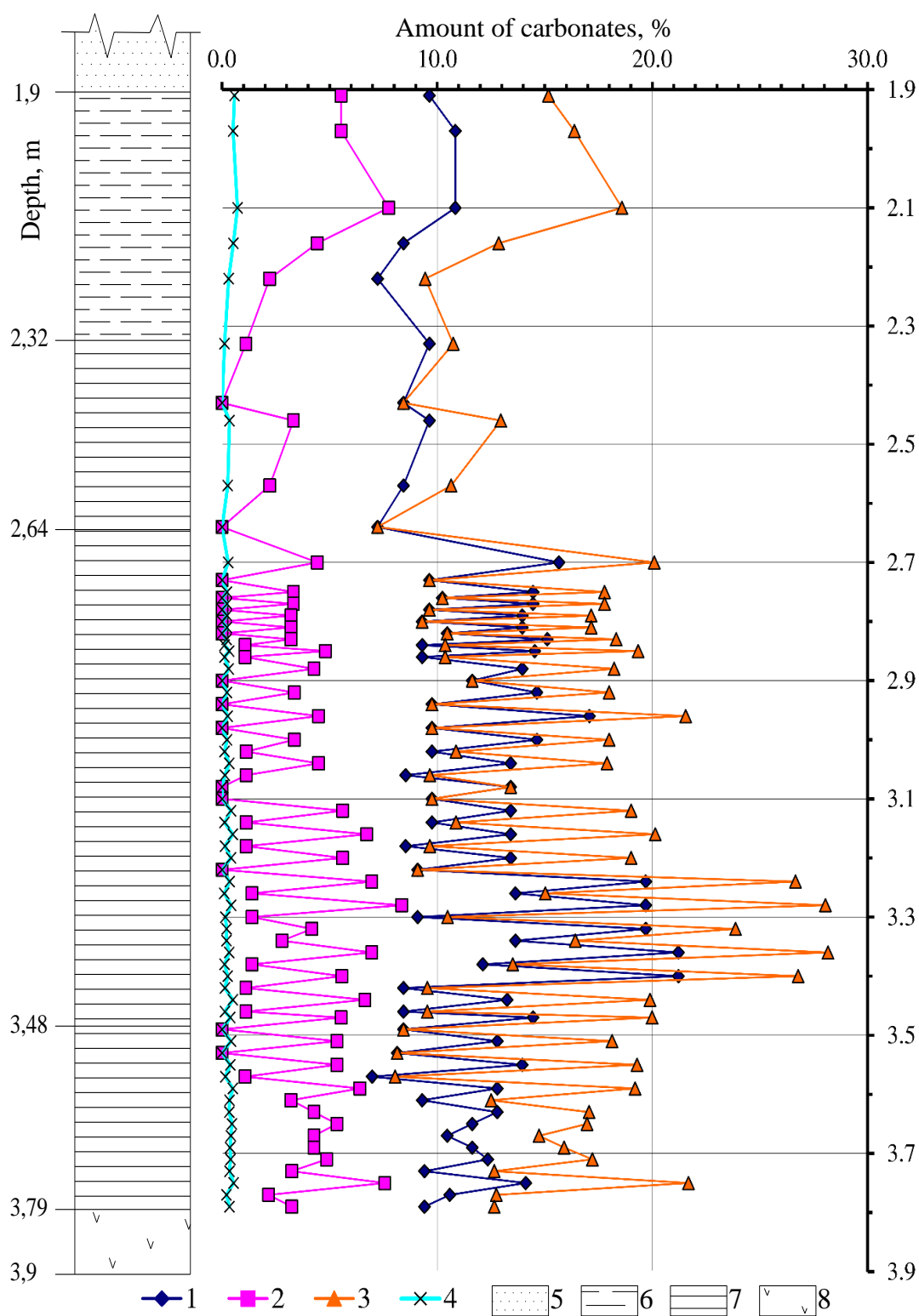


Fig. 30. Carbonates in the sediments of Meilès Sala outcrop: 1 – calcite, %; 2 – dolomite, %; bulk content of carbonates, %; 4 – dolomite vs calcite; 5 – sand; 6 – clay; 7 – varved clay; 8 – deluvium.

The seasonal character of the carbonate curves at a depth 3.73–3.51 m is inconspicuous. Sedimentation took place under the conditions of warmer climate (moderate winters and warm summers).

In the depth interval of 3.61–3.42 m, seasonality of carbonate curves is well defined, reflecting warm summers and cold winters.

Interval 3.42–3.22 m. The seasonal character of carbonate curves is well defined. The total of carbonates is higher. Dolomite is deposited even in cold seasons. This implies general climate warming.

Interval 3.22–3.10 m. The seasonal character of carbonate curves remains well defined though winters became warmer and dolomite was deposited even in colder time spans.

Interval 3.10–3.06 m. The carbonate curves show strong cooling as the glacier approached the basin. Deposition of dolomite ceased. The content of calcite also is lower.

Interval 3.06–2.98 m. The seasonal character of carbonate curves remains well defined though winters became warmer and dolomite was deposited even in colder time spans.

Interval 2.98–2.94 m. The variations of carbonate curves are more discriminate. At a depth of 2.96 m, there is a sharp increase of the total content of carbonates up to 21.55 % and calcite from 9.76 % to 17.07 %. The dolomite curve rises from 0.00 % to 4.48 % and again falls to 0.00 %.

Interval 2.94–2.74 m. The interval is marked by clearly defined seasonality of carbonate curves. Deposition of calcite and dolomite took place in warm time spans. In cold time spans, deposition of dolomite either took no place or was very slow.

Interval 2.74–2.64 m. At a depth of 2.70 m (No 61), the content of carbonates is discriminately higher (calcite from 9.64 % to 15.66 %, dolomite from 0.00 % to 4.436 %, total to 20.09 %), what implies considerable climate warming. It correlates with a considerably thicker (even 12.5 cm in thickness) stripe of sediments deposited in warm time span. As the warming is bound by zero quantities of dolomite curve on both sides it would be more correct to refer to this time span as a long warm summer.

Interval 2.64–2.32 m. This interval is affected by hypergenesis. The content of carbonates increases to 12.96 % in the sample of bluish clay with brownish tint (No 64)

taken from a depth of 2.46 m and decreases to 8.43 % in the sample (No 65) of red clay at a depth of 2.43 m. The trends of calcite and dolomite curves are similar. The difference is that the dolomite curve in this interval begins and ends on the zero graduation reaching its maximum at a depth of 2.46 m. The calcite curve varies from 7.23 % (No 62) to 9.64 % reaching its maximum at the same depth as dolomite. The total carbonate curve accentuates even more the climate warming during sedimentation at a depth of 2.46 m.

Interval 2.32–1.9 m. The content of dolomite slowly rises until at a depth of 2.10 m it reaches its peak (18.59 %) in the yellowish green clay sample (No 69) then falls down until at a depth of 1.91 m reaches 15.17 % in the green silty clay sample (No 71). The variations of calcite, dolomite and total carbonate curves are comparable. Seasonality is inconspicuous and the character of curves resembles carbonate variations during interglacials.

The last interval should be ascribed to the Merkinė interglacial whereas the older layers presumably formed under the conditions of intensive climate oscillations.

Carbonates in the sediments of Netiesos outcrop. Researchers agree that sediments of Merkinė interglacial are exposed in the Netiesos outcrop. The investigation history of this outcrop is described in detail in S. Būdėnaitė's (2007) postgraduate paper for master's degree and in S. Saarmann's (2012) publication. The newest data confirm this dating (Baltrūnas et al., 2013).

Carbonate distribution in the section is uneven. Their composition, content and content variation curves allow reconstructing the general features of climate conditions during sedimentation. The section is investigated from the bottom upwards, i.e. from the oldest to the youngest sediments.

Interval 21.70–20.80 m. Judging from carbonate curves, climate was rather warm without greater seasonal variations. The content of dolomite ranges from 6.72 to 14.56 %, calcite from 4.88 to 17.07 %. The total amount of carbonates is determined within the range 19.44–23.79 %. These values imply close to interglacial climate conditions (Fig. 31).

Interval 20.75–20.58 m. This interval shows a short change of sedimentation and climate conditions. The content of dolomite falls to zero, calcite and total carbonates to 7.32 %. This implies that colder water surged into the basin.

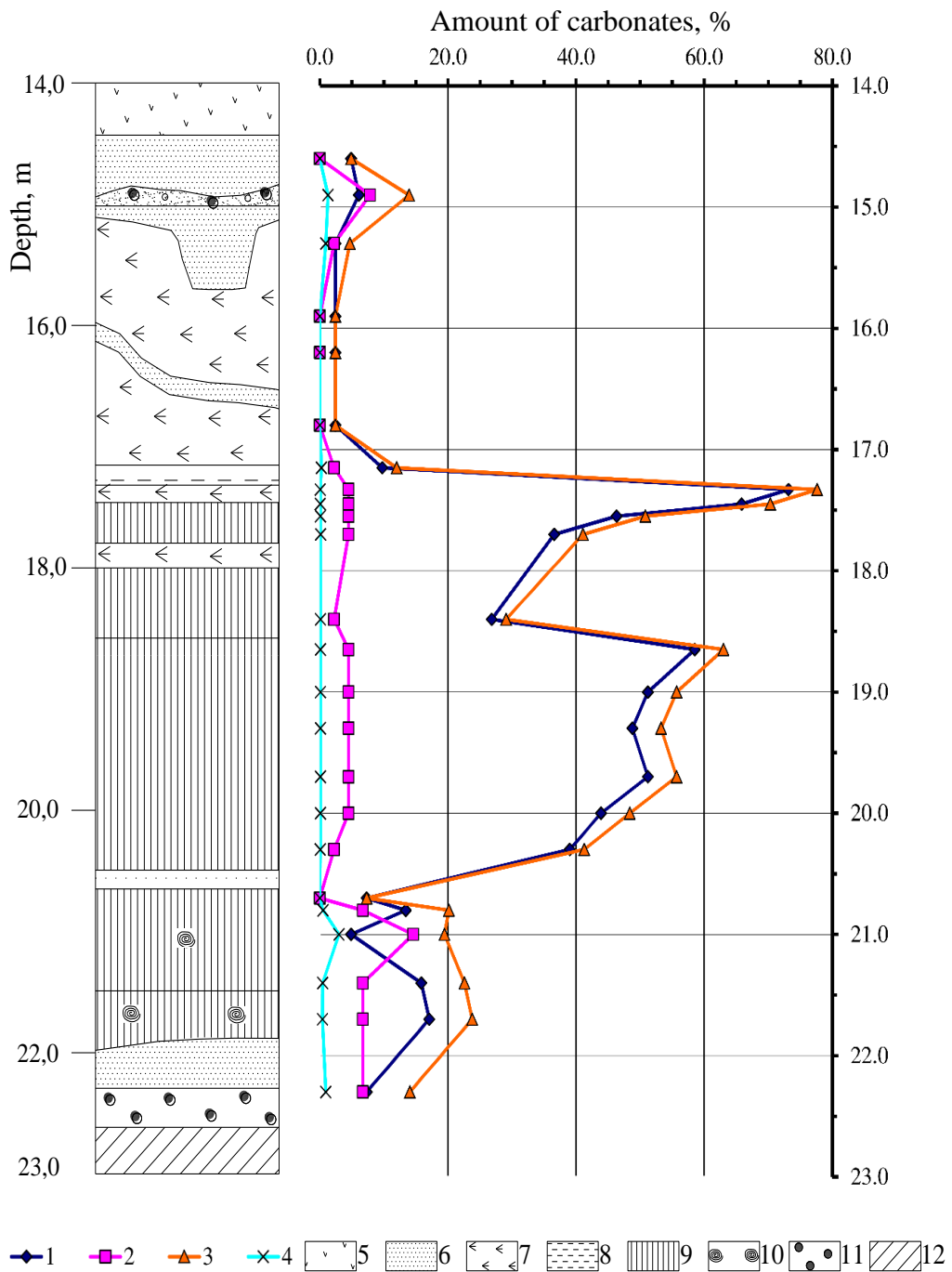


Fig. 31. Carbonates in the sediments of Netiesos outcrop: 1 – calcite, %; 2 – dolomite, %; 3 – total carbonates, %; 4 – dolomite vs calcite; 5 – deluvium; 6 – sand; 7 – peat; 8 – aleurite; 9 – gyttja; 10 – molluscs; 11 – gravel; 12 – morainic loam.

Interval 20.58–17.15 m. This interval is a combination of sediments with different lithology (Fig. 31.). The carbonate curves show a very pronounced time span of warm climate with two peaks and cooling to the lowest value at a depth of 18.40 m. The content of dolomite rises from 2.24 to 4.48 % (at a depth of 10.00 m), remains stable, falls to 2.24 % at a depth of 18.40 m and again rises to 4.48 % at a depth of 17.70 m, remains stable and falls to 2.27 % at a depth of 17.15 m. Calcite values are considerably higher. They vary from 39.03 % (at a depth of 20.30 m) to the first maximum 58.53 % (at a depth of 18.65 m), fall to 26.85 % (at a depth of 18.40 m), rise to 73.17 % (at a depth of 17.33 m) and complete the interval by 9.76 % at a depth of 17.15 m. The bulk content of carbonates varies from 41.26 % (at a depth of 20.30 m) to 55.70 % (at a depth of 19.70 m), reaches the first peak of 63.02 % (at a depth of 18.65 m), falls to 29.07 % at a depth of 18.40 m, again rises to 77.65 % at 17.33 m and falls to 12.00 % at 17.15 m.

Interval 17.15–15.90 m. The interval is composed of peat without dolomite (transport of terrigenous material did not take place). The content of calcite accounts for 2.44 %.

Interval 15.90–14.60 m. The variations of carbonate curves are inconspicuous and the quantities are low. Only at a depth of 14.90 m, the total content of carbonates reaches 13.94 %, dolomite 7.84 %, calcite 6.10 %, and again falls. This pattern of carbonate content implies rather cool climate.

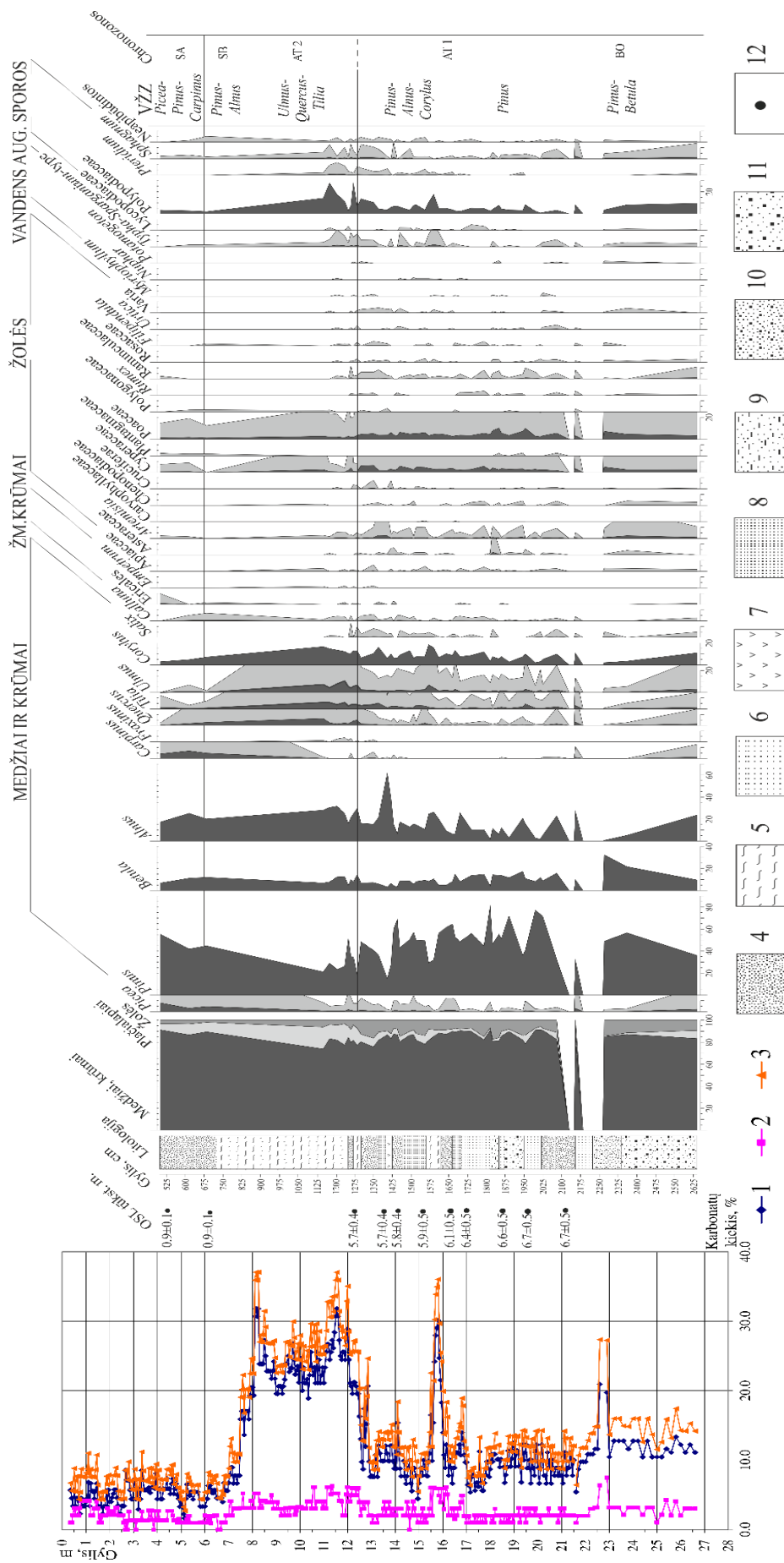


Fig. 32. Carbonates and percentage of pollen-spores in the sediments of borehole Nida VI: 1 – calcite, %; 2 – dolomite, %;

3 – total carbonates, %; 4 – fine-grained and tiny sand; 5 – sapropel; 6 – fine-grained sand; 7 – peat; 8 – tiny sand;

9 – sand with aleurite and sapropel; 10 – fine and medium-grained sand; 11 – badly sorted sand; 12 – OSL (ka),

*** Percentage of pollen-spores according to Alma Grigienė (2011).**

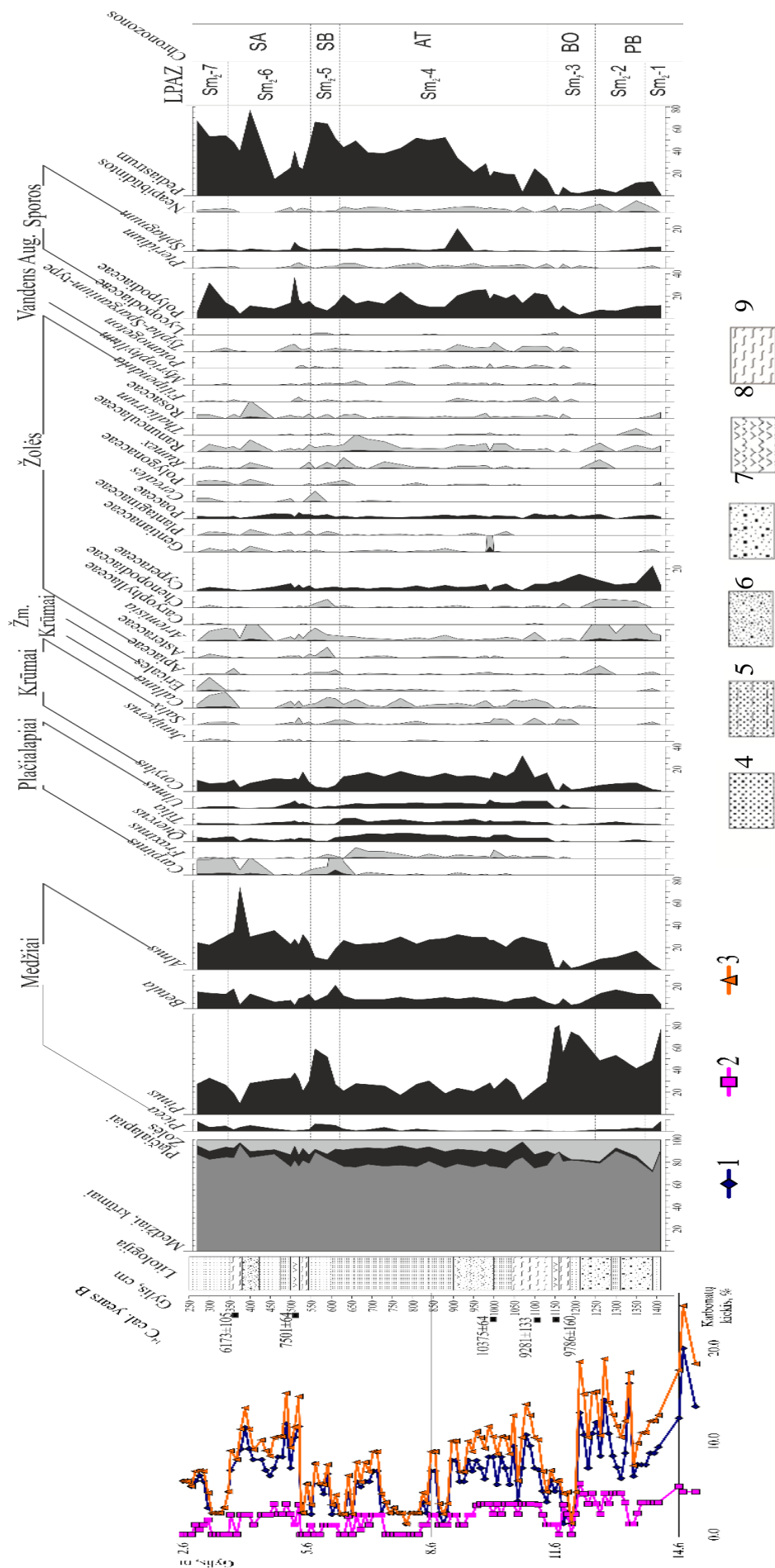


Fig. 33. Carbonates and percentage of pollen-spores in the sediments of borehole Smeltė-90c: 1 – calcite, %; 2 – dolomite, %;

3 – total carbonates, %; 4 – fine-grained sand; 5 – fine-grained organic sand; 6 – badly sorted sand; 7 – sand with gravel;

8 – peat; 9 – gytija.

* Percentage of pollen-spores according to Alma Grigienė (2011).

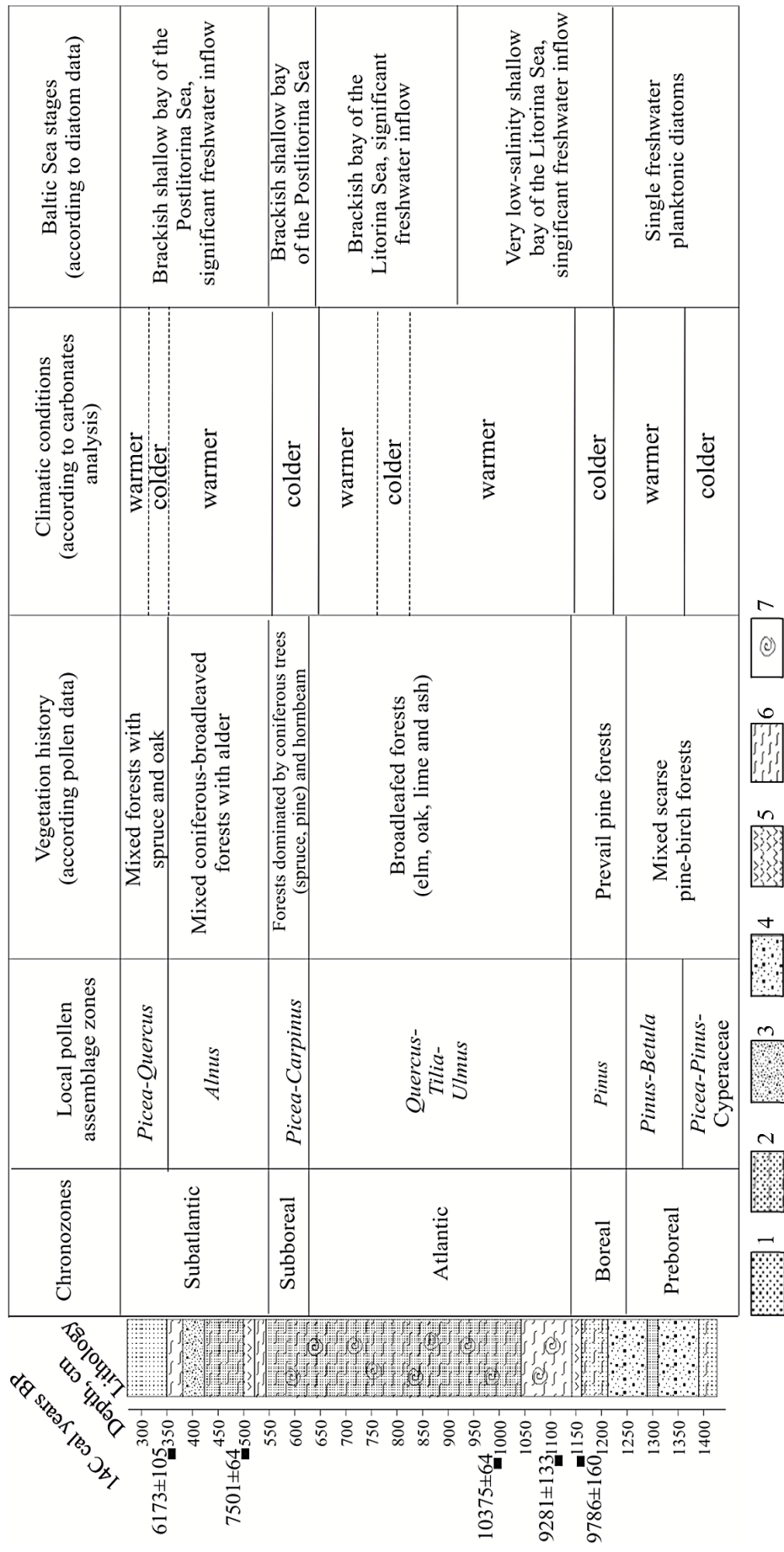


Fig. 34. Overview of climatic change events by the data from the section of Smelte-90c borehole: 1 – fine sand; 2 – fine organic sand; 3 – badly sorted sand; 4 – sand with gravel; 5 – peat; 6 – gyttja; 7 – molluscs.

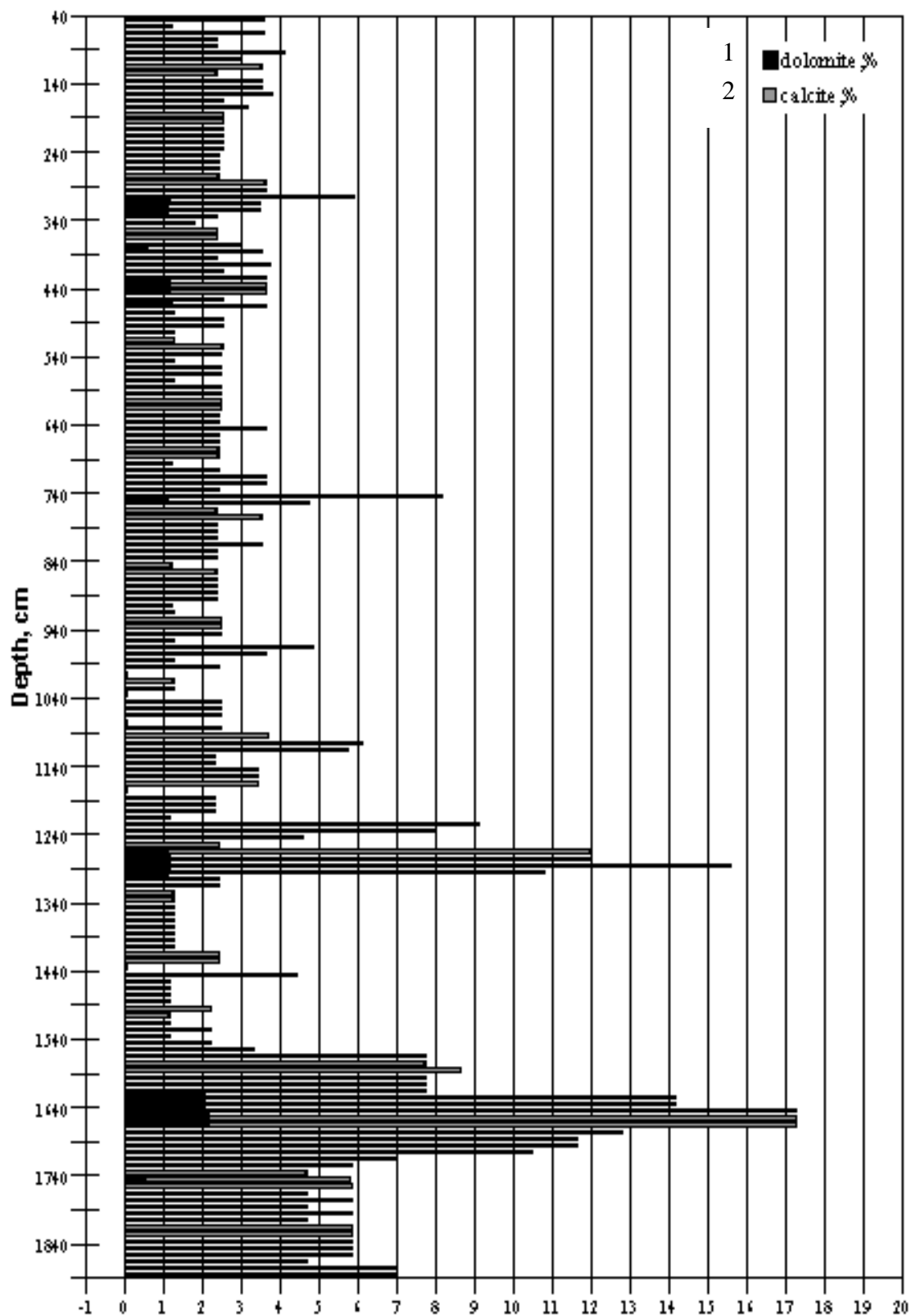


Fig. 35. Carbonates in the sediments of 65a borehole:

1 – dolomite, %; 2 – calcite, %.

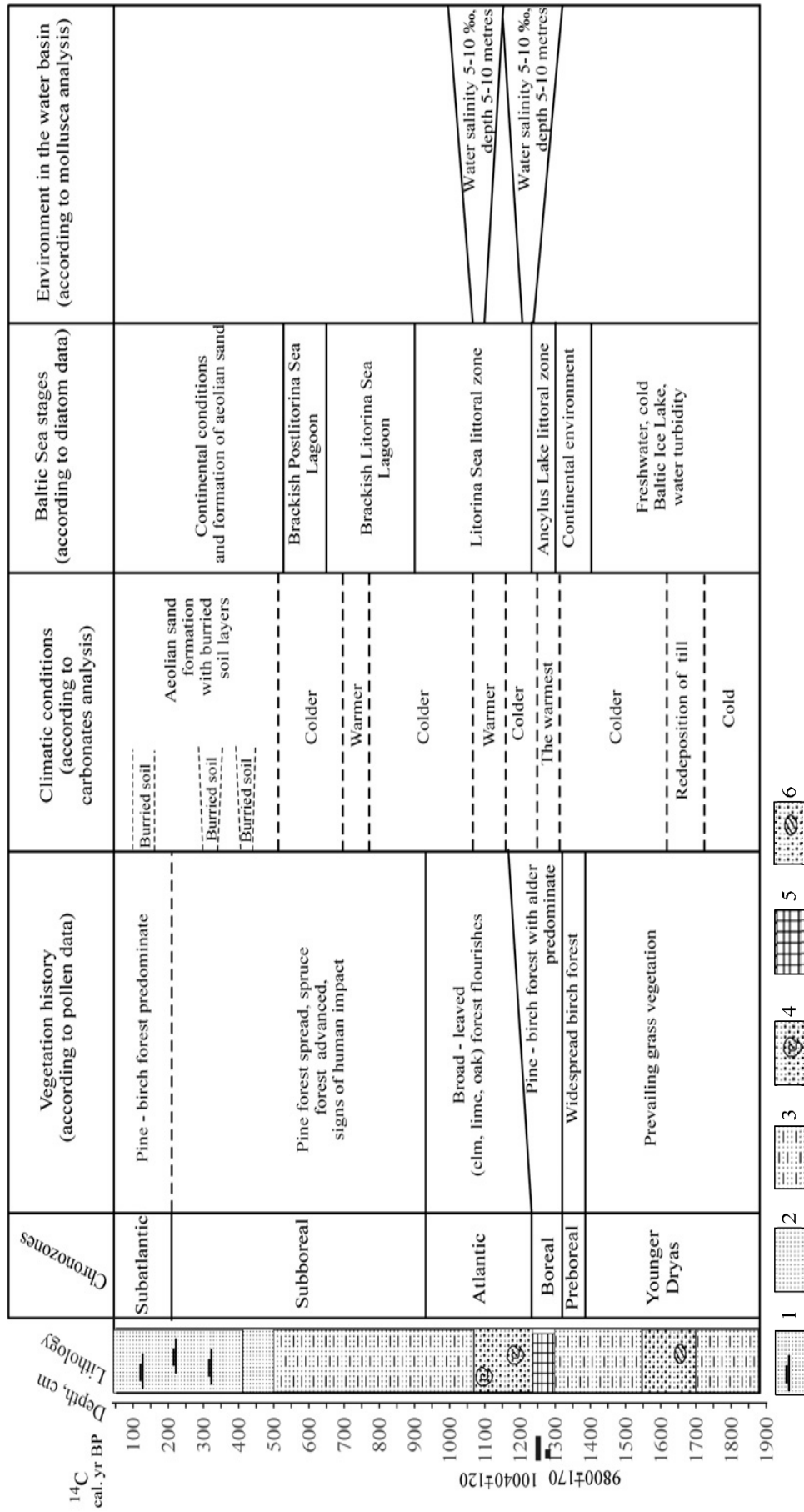


Fig. 36. Overview of climatic change events by the data from the section of borehole 65a:

- 1 – fine-grained sand with molluscs; 2 – fine-grained soil; 3 – fine organic sand;
- 4 – badly sorted sand with fragments of morainic loam.

In Preboreal, mixed scarce pine-birch forests prevailed in the western part of Lithuania. Climate was colder at the beginning of Preboreal and became warmer at the end. The absence of the Yoldia Sea deposits implies that the investigated area was the land at that time.

Dry pine forests were widespread during Boreal. Climate was relatively cold according to carbonates analysis. The level of Ancylus Lake was low and a shallow freshwater bay existed in the territory of the recent Klaipeda Strait.

Broadleaved forests were characteristic of Atlantic. Warm climate prevailed throughout the period; a short cold spell occurred only in the second half of Atlantic. Salinity of the Littorina Sea bay was very low because of large inflow of fresh water.

Coniferous trees were dominant in the Subboreal forests. Carbonates analysis data reflect a climate cooling event. Brackish Postlittorina Sea bay was very shallow because of dryer climate.

Mixed coniferous and broadleaved forests were widespread during Subatlantic. Climate was relatively warm with a short cooling event in the middle of the zone. Brackish Postlittorina Sea bay had large inflow of fresh water from the continent.

Formation of carbonates in heterochronous interglacials followed different patterns due to different climate conditions and different sequences of plant and organism development. The formation of Pleisocene carbonates progressed in correlation with changing climate conditions marked by specific features of different stages. The beginning and end of interglacials in sediment sections are characterized by noticeably lower carbonate values than the time spans of climate optimum. For this reason, the carbonate curves are in the form of chronologically progressing waves, which reflect the cyclic character of climate oscillations. One interglacial represents the largest cycle with a few (some) smaller cycles reflecting the sequence of plant evolution predetermined by climate changes.

The carbonate data about heterochronous non-glacial sediments were compared with the data of spores-pollen analysis. A direct correlation was observed between the variations of total carbonates and sequence of interglacial plant evolution predetermined by climate conditions. The maximal quantities of carbonates in the sections of heterogenous sediments correspond to the sequences of plants during the climate

optimum. Warming of climate reflected in the plant composition predetermined decrease of total carbonates.

When using carbonate values for interpretation of climate conditions during sedimentation it is important to bear in mind the general regime of the water basin reflected in the lithological composition of sediments. At times of deposition of coarser material, the content of carbonates may naturally increase due to a higher inflow of clastic material.

The percentage of total carbonates is in visual correlation with the data of pollen analysis: the increased values of thermophilous plants (*Quercus*, *Carpinus*, *Bettula*, *Tilia*) result in higher values of carbonates; the content of carbonates decreases with the spreading of plants of colder climate (*Pinus*, *Picea*, *Betula nana*, etc.). Therefore, this method allows evaluating climate oscillations (warmer and colder time spans) with greater accuracy.

The previously visually determined correlation links between the variation of carbonate distribution and spores-pollen data were statistically validated. The obtained positive and negative correlations reflect the actual climate oscillations.

Table 3.3.1. Correlation coefficients of carbonates and pollen.

Level of reliability $\alpha = 0.05$

	<i>Pinus</i>	<i>Quercus</i>	<i>Carpinus</i>	<i>Ulmus</i>	<i>Picea</i>	<i>Betulla</i>
Calcite	-0.58124	0.49667	-0.60498	0.77060	-0.73640	0.75185
Dolomite	-0.33457	0.40967	-0.62968	0.57483	-0.46645	0.81806
Carbonates	-0.33842	0.41795	-0.67880	0.58236	-0.47441	0.82028

A cyclic character of carbonate distribution of non-glacial deposits was determined. At the beginning of the interglacial, the content of carbonates is low. It reaches its maximal values during climate optimum and again decreases with the approaching next glaciation. The environments of retreating glacier contain relatively higher quantities of dolomite due to higher inflows of terrigenous material into the water basins.

Analysis of carbonates in non-glacial deposits in combination with other methods is recommended for use in reconstruction of palaeogeographic conditions of heterochronous Pleistocene interglacials and Holocene.

CONCLUSIONS

The goals achieved in the present study allow formulating the following conclusions:

1. Judging from the morphological features, carbonate class minerals dolomite and calcite in the Lithuanian Pleistocene tills are allochthonous, i.e. transported and accumulated by glaciers; autochthonous carbonates have not been detected in the investigated till layers.

2. The bulk content of carbonates in glacial deposits and the ratio d:c depend on the substratum rocks of different lithological composition exarated in the process of glacier advance. Therefore, these indices may serve as lithostratigraphic criteria for stratigraphic subdivision and correlation of palaeontologically “mute” Pleistocene tills.

3. According to distribution of carbonates in the Lithuanian Pleistocene sections, determined by statistical methods (Van der Waerden criterion), six inhomogeneous till layers were distinguished.

4. The boundaries of till layers determined by the data of carbonate analysis often are at variance with the boundaries distinguished by visual description according to the colour, which in itself cannot serve as a reliable criterion of stratigraphic correlation.

5. According to dolomite and calcite ratio, the tills can be ascribed to six stratigraphic units of different rank distinguished in the stratigraphic scheme of Lithuanian Quaternary; in the stratigraphic scheme, according to carbonate values, the most dolomite-rich till layer ($d:c=0.9-\geq 1$) is ascribed to the till of Medininkai glaciation.

6. The methods of stratigraphic correlation of glacial deposits, based on carbonate analysis and statistical processing of obtained, in combination with other research methods (geochronological and palaeobotanical) may contribute to more effective and reliable correlation of Pleistocene tills.

7. The composition, quantities and variation of quantities of carbonate minerals in non-glacial deposits reflect general climate characteristics during sedimentation.

8. The obtained correlation coefficients between carbonates and pollen data show a rather good and reliable link what is helpful in reconstructing palaeoclimate conditions of sedimentation as reflected in “mute” (without fossils) layers of deposits. The variations of the composition and content of carbonate material are in good correlation with the data of spores-pollen and diatomic analysis and reflect the variations of palaeogeographic conditions.

9. The beginning and the end of interglacials in the sections of interglacial deposits are characterized by noticeably lower quantities of carbonates than the time spans of climate optimum. For this reason, the curves of carbonate content have the form of chronologically progressing waves, which reflect the cyclic character of climate oscillations. One interglacial represents the largest cycle with a few (some) smaller cycles reflecting the sequence of plant evolution predetermined by climate changes.

LIETUVOS KVARTERO NUOGULŲ KARBONATINGUMASKAIP LITOSTRATIGRAFINIS KRITERIJUS IR PALEOKLIMATINIŲ SĄLYGŲ INDIKATORIUS

SANTRAUKA

Didžioji darbo dalis atlikta autorei studijuojant Vilniaus universiteto geologijos doktorantūros studijose (2012-2016 m.m.) bei vykdant su disertacijos tematika susijusias Vilniaus universiteto Geologijos ir mineralogijos katedros biudžetines temas bei Valstybinio mokslo ir studijų fondo (VMSF), vėliau - Lietuvos mokslų tarybos (LMT), finansuotus mokslininkų grupių projektus. Tyrimams medžiaga sukaupta iš Lietuvos teritorijoje išgrežtų gręžinių kerno bei čia sutinkamų upių atodangų.

Darbo teorinės prielaidos ir aktualumas

Kvartero nuogulų stratigrafinis suskirstymas ir koreliacija yra procedūra, leidžianti atskleisti kvartero storumės geologinę sandarą, suvokti jos formavimosi dėsningumus, atkurti vienu ar kitu kvartero periodo metu buvusias paleogeografines sąlygas, ir kt. Visa tai aktualu tiek Lietuvos, tiek ir aplinkinių regionų, turinčių panašią geologinę sandarą, tyrėjams. Kvartero stratigrafiam suskirstymui pagrindinio geologijoje naudojamo biostratigrafinio principo nepakanka dėl labai paprastos priežasties: didžioji dalis storumės – t.y. pleistoceno nuogulos - yra paleontologiškai „nebylios“. Geochronologiniai tyrimų metodai ne visais atvejais gali padėti spręsti iškilusias stratigrafines koreliacijos problemas dėl savo specifikos – vienais metodais galima datuoti tik gana jaunas nuogulas bei nuosėdas (pvz. radiokarboniniu metodu), kitų metodų galimybes riboja datavimui tinkamų nuogulų bei nuosėdų genetinių tipų spektras (pvz. liuminescenciniam datavimui netinka ledyninės kilmės nuogulos), ir pan. „Nebylių“ pleistoceno storumių koreliacijai tyrėjai paprastai naudoja įvairius litologinius kriterijus. Labiausiai išlaikyti ir geriausiai atsekami yra moreniniai sluoksniai, todėl pagal juos dažniausiai „nebylios“ storumės ir yra koreliuojamos. Tačiau morenų stratigrafines koreliacijos patikimumas labai priklauso nuo pasirinktų litostratigrafinių kriterijų ir jų pritaikymo galimybių. Tad naujų litostratigrafinių kriterijų paieška išlieka aktualia kvartero geologijos problema visuose kontinentinių apledėjimų paliestuose regionuose.

Lietuvos pleistoceno morenose nemažą dalį sudaro karbonatinga medžiaga, todėl karbonatų klasės mineralų, kaip potencialių litostratigrafinių kriterijų bei paleogeografinių sąlygų indikatorių, tyrimai ir tapo pagrindiniu darbo tikslu. Tad, atitinkamai, disertacinis darbas susideda iš dviejų dalių: pagrindinė skirta pleistoceno morenų karbonatingumo tyrimams ir efektyvių litostratigrafinių kriterijų išaiškinimui, kitoje – nagrinėjami karbonatų formavimosi ypatumai ir jų ryšys su klimatiniais pokyčiais tarpledynmečių sąlygomis. Vadovaujantis iki šiolei sukaupta ir publikuota informacija apie Lietuvos bei gretimų regionų kvartero geologinę sandarą, pokvarterinio substrato (prekvartero uolienų) litologinius ypatumus, pleistoceno kontinentinių ledynų dinamikos pobūdį, paleogeografinių sąlygų pokyčius ir kt., buvo iškeltos dvi pagrindinės darbo hipotezės: 1) ledynų paliktų moreninių nuogulų karbonatingumas bei kai kurių karbonatų klasės mineralų kiekio santykis turėtų atspindėti ledynų slinkimo kryptis, o tai galėtų tarnauti litostratigrafiniam „nebylių“ nuogulų stovyčių suskirstymui; 2) karbonatų sudėtis, kiekis bei kiekio kitimo pobūdis turėtų atspindėti neledyninių nuosėdų sedimentacijos metu buvusias klimatinės sąlygas, kas leistų iš dalies atkurti sedimentacijos metu buvusią paleogeografinę aplinką.

Šių hipotezių pagrindu buvo suformuluotas darbo tikslas ir sprendžiami uždaviniai.

Darbo tikslas ir uždaviniai

Darbo tikslas – įvertinti morenų karbonatingumo tyrimo duomenų panaudojimo galimybes Lietuvos pleistoceno stovymės stratigrafiniam suskirstymui ir koreliacijai bei paleogeografinių sąlygų rekonstravimui tarpledynmečiais ir poledynmečiu.

Pagrindiniai darbo uždaviniai yra šie:

1. Atlikti įvairiaamžių moreninių nuogulų karbonatingumo tyrimus bei gautų duomenų statistinę analizę.
2. Įvertinti galimybę ledyninių nuogulų karbonatingumo tyrimo duomenis panaudoti šių nuogulų stratigrafiniai koreliacijai; identifikuoti optimaliausius litostratigrafinius kriterijus.
3. Karbonatingumo tyrimo rezultatų pagrindu parengti morenų stratigrafinės koreliacijos metodiką pritaikant matematinius statistinius metodus.
4. Atlikti įvairiaamžių neledyninių nuosėdų karbonatingumo tyrimus siekiant nustatyti karbonatingumo sąsajas su sedimentacine aplinka ir klimato kaita.

Darbo naujumas

Karbonatingumo tyrimai kvartero ledyninėse nuogulose bei neledyninėse nuosėdose, nustatant ne tik bendrą karbonatų kiekį, bet ir karbonatų klasės mineralų kalcito ir dolomito kiekius atskirai, autorės atlikti savarankiškai bei išskirtinai pirmą kartą Lietuvoje.

Originalus autorės sprendimas litostratigrafiniu kriterijumi ledyninėms nuoguloms suskirstyti naudoti ne gautas absoliučias karbonatų klasės mineralų dolomito ir kalcito kiekių reikšmes, o jų santykį. Sukurta originali morenų stratigrafinės koreliacijos metodika panaudojant matematinius statistinius metodus (Van der Vardeno (*Waerden*) kriterijų).

Pirmą kartą Lietuvoje gauti karbonatų klasės mineralų kalcito ir dolomito bei bendro karbonatingumo kiekiai palyginti su palinologinių bei titnagdumblių tyrimų rezultatais.

Darbo teorinė ir praktinė reikšmė

Darbas papildo teorines žinias apie ledyninių ir neledyninių nuogulų bei nuosėdų sandarą, sudėtį, klimato kaitą jų formavimosi metu.

Svarbią reikšmę turi išskirtas litostratigrafinis kriterijus (dolomito ir kalcito santykis), tuo pagrindu sukurta įvairiaamžių morenų identifikavimo metodika tinkama plačiam naudojimui geologų moksliniuose darbuose, o taip pat pritaikoma praktiškai, ypač kvartero nuogulų geologinio kartografavimo darbuose.

Ginamieji teiginiai

Disertacinio darbo uždavinių sprendimas ir gauti tyrimo rezultatai leido suformuluoti šiuos ginamuosius teiginius:

- Karbonatų klasės mineralai – dolomitas ir kalcitas – Lietuvos pleistoceno morenose, sprendžiant pagal jų morfologijos ypatumus, yra alochtoniniai, t.y. pernešti ir akumuliuoti ledyno.
- Karbonatų klasės mineralų dolomito ir kalcito kiekio santykis ledyninėse nuogulose atspindi ledynų slinkimo kryptis ir gali būti litostratigrafiniu kriterijumi, naudojamu „nebylių“ nuogulų storymių (pleistoceno morenų) stratigrafinei koreliacijai.
- Karbonatų klasės mineralų sudėtis, kiekis bei kiekio kitimo pobūdis neledyninėse nuosėdose atspindi sedimentacijos metu buvusias klimato

sąlygas ir leidžia atkurti sedimentacijos metu buvusių paleogeografinių sąlygų bendrus bruožus.

Darbo pristatymas

Svarbiausi disertacijos darbo rezultatai pristatyti, aptarti ir svarstyti šiose mokslinėse konferencijose:

16. XI INQUA congress. Russia, Moscow, 1982 08 01-09.
17. International Conference and field symposium „Decoding the Last Interglacial in Western Mediterranean“, Sardinia, Italija, 2010 10 25-29.
18. XVIII INQUA congress: „Quaternary sciences – the view from the mountains“. Switzerland, Bern, 2011 07 21-27. [2 pranešimai]
19. International Conference and field symposium “Late Glacial Maximum in the Valday Region, NW Russia”. INQUA Peribaltic Working Group, Russia, 2012 09 13 – 17. [2 pranešimai]
20. „Jūros ir krantų tyrimai - 2013: 7-oji nacionalinė jūros mokslų ir technologijų konferencija“. Klaipėda, 2013 04 3-5.
21. International Conference and field symposium „Palaeolandscapes from Saalian to Weichselian, South Eastern Lithuania“. INQUA Peribaltic Working Group, Lithuania, 2013 06 25-30. [2 pranešimai]
22. VU Gamtos mokslų fakulteto Geologijos ir mineralogijos katedros metinė doktorantų konferencija „Nuo Žemės mantijos iki kvartero Lietuvoje“. Vilnius, 2013 11 28.
23. International Conference and field symposium „Late Quaternary terrestrial processes, sediments and history: from glacial to postglacial environments, Eastern and Central Latvia“. INQUA Peribaltic Working Group, Latvia, 2014 08 17- 22.
24. The 9th Baltic Stratigraphical Conference, Lithuania, 2014 09 8–9.
25. VU Gamtos mokslų fakulteto Aštuntoji mokslinė konferencija “Mokslas Gamtos mokslų fakultete“. Vilnius, 2014 10 03.
26. VU Gamtos mokslų fakulteto Geologijos ir mineralogijos katedros metinė doktorantų konferencija „Nuo silūro iki kvartero Lietuvoje“. Vilnius 2014 11 27.
27. XIX INQUA Congress: „Quaternary Perspectives on Climate Change, Natural Hazards and Civilization“. Japan, Nagoya, 2015 07 26 – 08 02. [2 pranešimai]

28. Kasmetinė Geologijos krypties doktorantų konferencija. VU GMF Geologijos ir mineralogijos katedra, Vilnius, 2015 11 19.
29. Tarptautinė konferencija „From Star and Planet Formation to Early Life“. Vilnius, 2016 04 25–28.
30. International Conference and field symposium „Quaternary geology of north-central Poland: from the Baltic Coast glacial to the LGM limit“. INQUA Peribaltic Working Group, Poland, 2016 08 28- 09 02.

Publikacijos

Doktorantūros studijų metu gauti tyrimų rezultatai publikuoti moksliniuose žurnaluose ir kituose leidiniuose: 4 publikacijos - ISI Web of Science žurnaluose, 3 - ISI Master List žurnaluose, 1 - kituose recenzuojamuose žurnaluose, 1 - tarptautinių konferencijų leidiniuose, 1 - kituose leidiniuose. Publikacijų sąrašas pateiktas skyriuje „Autorės publikacijų bei mokslo projektų sąrašas“.

IŠVADOS

Sprendžiant disertacinio darbo uždavinius gauti tyrimo rezultatai leidžia suformuluoti tokias išvadas:

1. Karbonatų klasės mineralai – dolomitas ir kalcitas – Lietuvos pleistoceno morenose, sprendžiant pagal jų morfologijos ypatumus įvairiose granulimetrinėse frakcijose, yra alochtoniniai (pernešti ir akumuliuoti ledynų); autochtoninės kilmės karbonatų tirtose morenose nerasta.

2. Ledyninių nuogulų bendras karbonatingumas bei dolomito ir kalcito santykis priklauso nuo ledyno slinkimo metu egzaruotų skirtingos litologinės sudėties substrato uolienu; dolomito ir kalcito santykis gali būti litostratigrafiniu kriterijumi stratigrafiškai suskirstant ir koreliuojant paleontologiškai „nebylias“ pleistoceno morenas.

3. Pagal karbonatų pasiskirstymą Lietuvos pleistoceno pjūviuose išskiriama, naudojant statistinius metodus (Van der Vardeno kriterijų), iki 6 tarpusavyje nehomogeniškų moreninių sluoksnių.

4. Moreninių sluoksnių ribos pjūviuose, nustatytos pagal karbonatingumo tyrimų duomenis, dažnai nesutampa su tų pačių moreninių sluoksnių ribomis, išskirtomis pjūvio vizualinio aprašymo metu; pastaruoju atveju sluoksnių išskyrimo pagrindu daugeliu

atvejų yra nuogulų spalva, kuri negali būti patikimu stratigrafinės koreliacijos kriterijumi.

5. Pagal dolomito ir kalcito santykį morenas galima priskirti 6-iems skirtingo rango stratigrafiniams vienetais, išskiriamiems Lietuvos pleistoceno stratigrafinėje schemoje; pagal karbonatingumo rodiklius labiausiai dolomitingas moreninis sluoksnis ($d:k = 0,9 - \geq 1$) stratigrafinėje schemoje priskiriamas Medininkų apledėjimo morenai.

6. Ledyninių nuogulų stratigrafinės koreliacijos metodika, paremta šių nuogulų karbonatingumo tyrimų ir jų statistinio apdorojimo duomenimis, gali padėti, ją taikant kompleksiskai su kitais tyrimų metodais (geochronologiniais, paleobotaniniais), kur kas efektyviau ir patikimiau sukoreliuoti pleistoceno morenas.

7. Karbonatų klasės mineralų sudėtis, kiekis bei kiekio kitimo pobūdis neledyninėse nuogulose atspindi sedimentacijos metu buvusius bendrus klimato bruožus.

8. Gauti koreliacijos koeficientai tarp karbonatingumo ir palinologinių duomenų rodo esant pakankamai gerą ir patikimą ryšį – tai suteikia galimybę atkurti buvusias klimato sąlygas ir iš „nebylių“ (neturinčių fosilijų) storymių. Karbonatinės medžiagos sudėties ir kiekio kaita gerai koreliuojasi su palinologinių ir titnagdumblių (diatomėjų) tyrimų duomenimis bei atspindi paleogeografinių sąlygų kaitą.

9. Tarpledynmetinių nuosėdų pjūviuose tarpledynmečio pradžia ir pabaiga charakterizuojama ženkliai mažesniais karbonatų kiekiais nei klimatinio optimumo laikotarpiai, todėl karbonatų kiekio kreivės turi bangos, „sklindančios“ laike, formą bei atspindi paleoklimato kaitos cikliškumą. Stambiausią ciklą sudaro vienas tarpledynmetis, kuriame galima išskirti kelis (keletą) smulkesnių ciklų, atspindinčių konkretaus tarpledynmečio augalijos raidos seką, nulemtą klimato sąlygų kaitos.

Darbo apimtis ir struktūra

Daktarinį darbą sudaro įvadas, 3 skyriai, išvados, panaudotos literatūros šaltiniai, autorės publikuotų darbų bei mokslo projektų sąrašas.

Disertantės mokslinių publikacijų disertacijos tema sąrašas pateiktas atskirame skyriuje. Literatūros sąrašė nurodyta 136 naudotos literatūros šaltiniai. Darbo apimtis - 151 puslapis su 65 paveikslais ir 17 lentelių.

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APPENDICES

Appendix 1

PARTICIPATION IN RESEARCH PROJECTS

- „Kvartero nuogulų sedimentacijos sąlygos ir stratigrafija“ 2011-15 metai – Geologijos ir mineralogijos katedros vykdoma biudžetinė tema, vad. dr. G.Vaikutienė. [*„Sedimentology and stratigraphy of Quaternary deposits”*. *Projects Supported by University Budget*]
- „Baltijos jūros priekrantinės ir giliauvidurinės zonų vėlyvojo ledynmečio ir holoceno nuosėdų sedimentologinių ir paleobotaninių tyrimų duomenų koreliacija“ 2006-10 metai. Geologijos ir mineralogijos katedros biudžetinė tema, vad. habil.dr., prof. A.E.Trimonis. [*“Correlation of the sedimentological and palaeobotanical data of Late Glacial and Holocene deposits in shallow and deep water zone of Baltic Sea.”* *Projects Supported by University Budget*]
- „Paleogeografinių sąlygų raida Lietuvoje poledynmetyje Baltijos jūros ir sausumos sąveikoje“ (POLEDYNMETIS LIETUVOJE), Lietuvos mokslo taryba, Lietuvos mokslo tarybos nacionalinė mokslo programa „Ekosistemos: klimato kaita ir aplinkos poveikis“, 2010-08 – 2011-12, sąmatinė vertė - 696.76 tūkst. Lt (sutartis LEK- 03/2010). [*National Science Programme “Lithuania ecosystems: climate change and human impact” project “Palaeogeographical changes in Lithuania throughout the Postglacial time under the Baltic Sea and land interaction (POLEDYNMETIS LIETUVOJE)” (LEK-03/2010).*]
- „Klimato staigių kitimų ir senvaginėse nuogulose palaidotos medienos geochronologinis įvertinimas“ – Valstybinis mokslo ir studijų fondas, 2009 metais, sąmatinė vertė – 36 700 Lt. (*maksimali galima – 40 000Lt*) (sutartis Nr. T-84/09). [*Project (supported (LSSF): “Geochronological estimation of sudden climatic changes and buried woods in oxbow lake sediments“*]
- „Ekstremalūs gamtos reiškiniai ir paleoklimato kitimai per pastaruosius 15 000 m. Lietuvoje“ – Valstybinis mokslo ir studijų fondas, 2008 metais (sutartis T-37/08), sąmatinė vertė-34 000 Lt; (*maksimali galima – 40 000Lt*). [*Project (supported (LSSF): “Extreme natural phenomena and palaeoclimatic changes during the last 15 000 years in Lithuania“*].

POPULAR SCIENCE ARTICLES:

- Rudnickaitė Eugenija.** 2015. The Collections of the Mineralogy Cabinet of Vilnius University in the Vilnius Museum of Antiquities [Vilniaus universiteto Mineralogijos kabineto rinkiniai Vilniaus senienų muziejuje]. - *The Struggle for History: The Vilnius Museum of Antiquities (1855-1915) [Kova dėl istorijos: Vilniaus senienų muziejus (1855-1915)]*. International scholarly conference, Vilnius 7-8 May 2015 [Tarptautinė mokslinė konferencija, Vilnius, 2015 m. gegužės 7-8 d.]. Lietuvos nacionalinis muziejus, p. 97-98. (ir pranešimas).
- Rudnickaitė Eugenija.** 2014. Neformalaus gamtamokslinio ugdymo varomoji jėga: ką gali vienas žmogus? *Gamtamokslinis ugdymas bendrojo lavinimo mokykloje - 2014 = Natural science education at a general school - 2014: XX nacionalinė mokslinė-praktinė konferencija*, 2014 m. balandžio 25-26 d. Panevėžys. (pranešimas)
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- Pastaba:** daug pranešimų daryta geologijos mokslo populiarinimui mokiniams, mokytojų konferencijose; ekskursijos, mokslo populiarinimo renginiai VU Geologijos muziejuje.

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