II INTERNATIONAL SYMPOSIUM

CLAYS AND CERAMICS

BOOK OF ABSTRACTS

UNIVERSITY OF LATVIA,
ACADEMIC CENTRE FOR NATURAL SCIENCES
29–31 JANUARY 2018

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II International Symposium “CLAYS AND CERAMICS”. Book of Abstracts. University of Latvia. 2018, 84 p.

Symposium CC2018 is held within the framework of the University of Latvia 76th International Scientific Conference and is notable for giving insight into versatile, topical and applied research on clays and ceramics. The Book of Abstracts features abstracts allowing to recognize notable researchers, their studies and achievements, thus encouraging and supporting the researchers of other fields to join in this broad research area.

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RESPROD

This publication was financially supported by the National Research Program “ResProd” No. 2014.10-4/VPP-6/4.1 project “GEO”

Language editor: Daina Ostrovska
Computer graphics and design: Baiba Lazdiņa

ISBN 978-9934-18-304-1

FOREWORD

Welcome to the 2nd International Symposium "Clays and Ceramics 2018". On behalf of organizing committee, we would like to express our gratitude to all of you who have supported us for this project to come true. We sincerely thank our main partner University of Latvia and specially Professor Valdis Segliņš for his personal encouragement and support, which was crucial for our team. We are also grateful to Sietronics/SiroQuant for sponsoring the event. Latvian Clay Group is very honoured for the presence of the President of AIPEA, Professor Reiner Dohrmann, and we thank him for his enthusiasm and support in organizing the Clay meetings in Northern Europe. Special thanks to the French Clay Group and its members Jocelyne Brendlé and Lionel Limousy, as well as Mejdi Jeguirim for their support in organizing the special issue of the Comptes Rendus Chimie devoted to this symposium. Many thanks to our friends and colleagues from Estonia, Russia, Lithuania, Sweden, Algeria, France, Germany and Croatia for their participation.

We have chosen to organize the symposium program in four parts. The first session will be devoted to the environmental aspects of clays in geology and modern soils. The second session features talks about the clay-based composite materials. In the third part of conference we have regrouped talks about the diffusion, sorption and cation exchange processes involving clay minerals. Finally, the fourth session will be about clays in archaeology and arts.

Do not miss the chance to visit the exposition featuring artwork from clays by Ieva Bertašiūtė Grosbaha and the exposition about Latvian clay scientists near the conference room prepared by the librarians of Natural Sciences of the University of Latvia R. Alkšbirze, E. Sniedze and A. Pūcēna.

We wish you productive scientific discussions during the conference and enjoyable stay in Riga.

Līva Dzene and Ilze Vircava

CONTENT

WEATHERING TRACERS OF THE ENVIRONMENTAL CHANGES ACROSS THE ARCHEAN AND PROTEROZOIC TRANSITIONS IN EARTH HISTORY

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Weathering is a controlling factor in so-called "Critical Zone", the near-surface environment where water, rock, air, and life meet in a dynamic interplay that generates soils, sustains ecosystems, and shapes landscapes [1]. This, in turn, allows quantification of feedbacks between climate, tectonics and weathering over billions of years on Earth and beyond.

Paleosols as remains of ancient soils are of special interest for understanding the coevolution of atmosphere/litosphere in symbiosis with biota [2]. The weathering has played intriguingly important role in the evolution of Earth hallmarked with two milestones. First, the Archaean-Proterozoic transition when Great Oxygenation Event (GOE) occurred at 2.3 Ga [3]. Secondly, the Proterozoic-Phanerozoic transition (ca 1.0–0.5 Ga) marked by significant environmental changes: reconstruction of biogeochemical cycles, global glaciations followed by transient greenhouse periods, final oxygenation of atmosphere and the emergence of multicellular animal life; however, mechanisms behind all these changes are still heavily debated.

Oxygenation of the atmosphere during GOE when the O_2 reached 1 % of the present atmospheric level (PAL) caused significant enhancement in continental weathering rates by oxidation of terrestrial sulphides and formation of acidic surface waters, and boost in nutrients inflow to the oceans. GOE was followed by a poorly explained collapse in atmospheric O_2. Mn-leaching of paleosols and Cr-isotope signatures suggest level of atmospheric O_2 in the Mesoproterozoic as low as < 0.1 % PAL [4]. These conditions might have lasted until early Neoproterozoic (1.0–0.8 Ga) when Neoproterozoic Oxygenation Event [2] started as suggested by significant shifts in oceanic chemistry [5].

I review and discuss the weathering indicators as recording the environmental conditions across these important time-periods in the Earth

Acknowledgments:
This study was financed by Estonian Research Council grant PUT1511P.

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NEW CLAY CERAMIC MATERIALS

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Clays are one of important rocks on our planet and one of most widely used raw material for the production of varied ceramic articles. Ceramic production history is well known since the beginning of human development. Diversity of ceramic articles and products is established by variety of clays and clay minerals in these rocks.

1:1 clay mineral kaolinite containing clays are used for the production of refractory materials in the thermal treatment kilns, and some other heat-resistant products are used as well. In the structure of kaolinite neither tetrahedral nor octahedral sites have isomorphic substitution of Si^{4+} or Al^{3+} ions, respectively, and the properties of obtained materials have been influenced only by various admixture in kaolin. However, some isomorphic substitution of Mg^{2+}, Fe^{3+}, Ti^{4+} and V^{3+} for Al^{3+} can occur in octahedral site. In the oil cracking technology kaolin as catalyst is used.

More complicated is the question about hydromicas. Hydromicas such as hydrobiotite and hydromuscovite have large amount of various substitution both in the tetrahedral and octahedral sites that influences not only the structure and properties of the same minerals but also the properties of ceramic materials produced from hydromica containing clays. The identification of hydromicas phases by use of XRD phase analysis is problematic. Wide variety of ceramic materials has been produced from hydromica containing clays. The deciding factor when using clay in ceramic technology is not only the type and structure of the same hydromica, but also presence of various admixtures in the natural clays. The sintering temperature of clay is the most important practical property in the ceramic technology that determines real firing temperature and properties of articles. The sintering temperature depends on substitutions in the structure of minerals and admixture type. The 2:1 clay mineral structure and admixture in the natural clay are influenced by geological conditions, it means – the age of clay sediments.

In Latvia there are two clay types: the oldest is Devonian (age ~495 million years) and the youngest is Quaternary clay (age about 70000 years). Illite has been the main clay mineral in these clays but they contain also 5–15 % of kaolinite. The amount and type of admixtures is the general difference between these clays. Devonian clays are called lime less clays and the main admixture is quartz sand and 5–9 % of very small iron (III) oxide in the form of thin layer on the clay or sand particles. Red, light or purple colour is the characteristic sight of this clay, and ceramic articles after sintering are coloured red. Quaternary clays differ from the Devonian with admixture of alkaline earth metal carbonates in the amount of up to 20 %. The amount of clay fraction (particle diameter < 0.005 mm) in average ≥ 70 % is the second important difference between Latvia's clay types. The content of iron oxide in the Quaternary clays is lower and Fe^{3+} ions mainly are bounded in the octahedral site of illite. It determines the colour of Quaternary clays – brownish, but the colour of articles after sintering depends on the sintering temperature and the amount of carbonates in the raw clays. The colour of ceramic articles depends also on the environment in the sintering kiln. Creation of reducing environment in the end stage of sintering leads to the formation of dark coloured surface.

Despite the fact that the history of ceramic is very ancient, the possibility to create ceramic materials with new properties and for other uses is very urgent today. Porous ceramic materials for environmental technology are used in a variety of ways such as filters, sorbents or catalyst. Lightweight material pellets of expanded clay are well known thermal insulating filler in the technology of concrete. Technology of production is multi-stage and energy-intensive. A new one-stage production technology has been developed by enlarging traditional basis of raw illite clay materials and reducing of production time [1]. The possibility to produce expanded clay pellets with variable properties and various use has come around. There are pellets with apparent density of 0.53 g/cm^3 that can float on the surface of water a long time and serve to collect contaminants on the surface of water reservoirs. A new type of ceramic sorbent has been developed on the basis of new expanded clay technology. The raw materials are iron oxide containing illite clays and additive of large amount of crushed wood. The material has been produced by very fast thermal treatment of dried pellets. The structure of porous pellets is formed of two parts – porous ceramic shell and black core that contains predominantly carbon. The thermal treatment temperature is lower than the temperature that characterizes full dehydroxilation of illite. A change of crystalline phases has been determined by XRD analysis and some shift of diffraction lines that characterize the basal plates of dioctahedral illite have been detected. The obtained material combines two types of sorbents: activated carbon with large specific surface area and characteristic physical sorption, and porous ceramic with a smaller specific surface area but physical and possible chemical sorption. The obtained materials characterize large specific surface area and BET analyses shows the presence of nanosize pores (Fig. 1). Pyrolysis of wood particles in the presence of clay minerals in the hydrothermal condition inside pellets is a driving force for obtaining such sorbent and catalytic influences of illite on this process. A sorption ability and speed depends on the type of raw illite clay.

Catalytic influence of 1:1 clay mineral kaolinite has been detected in the ceramic processing. Highly porous oxide ceramic has been obtained by casting

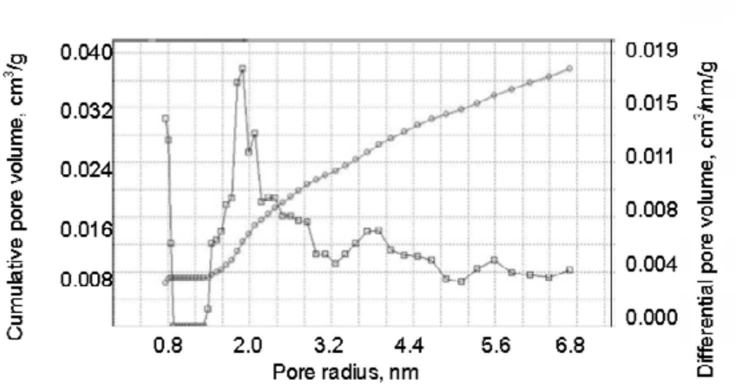

Fig.1. Pore size distribution in the Devonian clay ceramic containing activated carbon.

concentrated suspension of metal oxides and kaolin by additive of small amount of aluminum powder. Pore formation in the suspension and during thickening and solidification has happened as a result of chemical reaction between aluminum powder and water with elimination of hydrogen [2]. The cause of the reaction is the contact between charged kaolinite particles (zeta potential −19,8 mV) and aluminum particles with following corrosion of metal. In the dried samples XRD analysis confirmed the presence of kaolinite without any changes. Similar process has been detected in the concentrated suspensions of illite clay by additive of kaolin. Obtaining of highly porous clay ceramic by this method was influenced by the type of illite clay. Quaternary illite clays with admixture of carbonates are not valid for the production of highly porous ceramic in such way. The presence of carbonates in clays influences viscosity of suspension, whereas the presence of Ca^{2+} ions thickens the suspension and delays the formation of homogeneous pore structure in the material.

Acknowledgements:
Investigation of clay and clay ceramic has been carried out in the framework of National Research Program "ResProd" project "Investigations of land recourses and new products and technologies".

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CRYSTAL-CHEMICAL VARIATIONS IN K-DIOCTAHEDRAL MICAS 1M: DISTINGUISHING FEATURES AND IDENTIFICATION CRITERIA FROM XRD AND FTIR DATA

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Isomorphous cation substitutions in the tetrahedral and octahedral sheets typical for micas in general are especially diverse in low-temperature potassium dioctahedral micas. K-dioctahedral 1*M* micas, which are abundant in various geological environments, form two intersecting isomorphous series: Fe-poor varieties range in composition from (Mg, Fe)-poor illite to aluminoceladonite through Mg-rich illite, and Fe-bearing varieties, from illite to celadonite through Fe-illite, Al-glauconite and glauconite. The high degree of crystal-chemical heterogeneity, as well as the ambiguity in conventional nomenclature, complicate the identification of these mica varieties.

To reveal the structural and crystal-chemical variability in K-dioctahedral 1*M* micas and to define the composition ranges and identification criteria for the mica varieties in the two series, a collection of samples of various compositions was studied by X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy. The results and implications for Fe-poor mica varieties are treated in detail in [1] and will be covered in brief, the main attention being focused on Fe-rich micas.

Analysis of the relationships between unit-cell parameters and cation composition showed that the Fe-rich mica series includes four groups: Fe-bearing illites, Al-glauconites, glauconites, and celadonites, each characterized by a specific combination of unit-cell parameter variation ranges. The illite group contains two distinct subgroups: Fe-bearing Mg-rich illites and Fe-illites, which differ not only in cation composition variation ranges, but also in FTIR characteristics. The results obtained suggest a revision in the conventional mica classification, so that illites should be characterized by the ratio of octahedral Al to the total amount of trivalent octahedral cations, $K_{Al} \geq 0.65$. In addition, a revised nomenclature should take into account the subdivision of the illite group into illites proper and Fe-illites, as well as the existence of mica samples of Al-glauconite composition.

The boundary between Fe-illites and Al-glauconites corresponds to K_{Al} between 0.60 and 0.65 and occurs at $b \sim 9.05$ Å. The partially overlapping variation ranges of cation composition and cell parameters may complicate the distinction between Al-glauconites and glauconites, which can still be unambiguously differentiated using FTIR data. The dramatically different XRD and FTIR characteristics confirm that glauconite and celadonite should be treated as separate mineral species. The distinctive features of celadonite are relatively low values of $c\sin\beta$ and reduced $|c\cos\beta/a|$ in combination with b parameters that are lower than those for glauconites and similar to those for Fe-illites, as well as the sharp absorption bands at specific positions in the Si-O and OH stretching regions of FTIR spectra.

Acknowledgments:
The author is deeply grateful to Victor A. Drits, Boris A. Sakharov, Tatiana A. Ivanovskaya, Olga V. Dorzhieva (Geological Institute, RAS, Moscow, Russia), and Douglas K. McCarty (Institute of Geological Sciences, PAS, Krakow, Poland).

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SESSION: CLAYS ENVIRONMENTAL ASPECTS IN GEOLOGY AND MODERN SOILS

NEOPROTEROZOIC WEATHERING CRUST OF BALTIC BASIN

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The Neoproterozoic, ca 560–600 Ma old weathering crust is developed on a major disconformity in eroded Paleoproterozoic-Mesoproterozoic metamorphic-plutonic crystalline basement and is overlaid by unmetamorphosed Ediacaran sandstones-claystones. Paleosol is accessed in more than 100 drillcores where the thickness of the alteration varies from few meters to exceptional 150 m on fractured alumo-gneiss parent rocks. Paleosol is preserved unmetamorphosed, but probably slightly modified by K-metasomatosis (diagenetic illitization), and the uppermost part of most weathering profiles is partially eroded. This kind of thick, well preserved lateritic kaolinite-rich weathering profile with hematite/goethite rich duricrust is similar to modern oxisols and most likely formed in warm and humid climate [1], [2].

Understanding Precambrian paleosol profiles provides important and direct evidence of the past climate (temperature, precipitation), atmospheric composition ($p\mathrm{CO}_2$, $p\mathrm{O}_2$) and (microbial)biota. One of the major variables in soils is pH that controls the type and abundance of cations in solution and nutrient availability. However it is not possible to measure pH directly in paleosols. Recently a new pedotransfer function for estimated soil pH in paleosols based on bulk geochemistry was proposed by Lukens et al. [3]. The molecular ratio of aluminum to aluminum plus calcium (AlCa) was found to describe the paleo-pH values. The AlCa function of Baltic paleosol profiles show a vertical acidic to moderately alkaline pH gradient. Across the soil-rock weathering transition the estimated pH values at soil surface are ~5.5 and increase to ~8 with depth. The results are in agreement with the pH predictions of aluminum phosphate-sulphate

(APS) minerals. The APS minerals reflect down profile pH changes from acidic (<6) in the uppermost few metres in the APS precipitation zone, to neutral or near neutral at 4–5 m-depth from the paleoweathered surface [4].

Acknowledgments:
This study was financed by Estonian Research Council grant PUT1511P.

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CHEMICAL LEACHING ON LAND AT ARCHEAN–PROTEROZOIC TRANSITION

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Oxygenation of the atmosphere ca 2.3 Ga ago principally changed the redox state of the Earth's near-surface environments. Oxidation possibly intensified the weathering of rocks exposed on continents and increased mobility of some indicative elements dissolved under oxidative attack. Particularly, the oxidative weathering of sulphide minerals resulting in sulphuric acid as the by-product of oxidation has been viewed as a driver of strong acidic weathering, and causing delivery of sulphate into the oceans. The oxidation of the atmosphere caused changes in continental weathering which eventually resulted in build-up of sulphate reservoir and dawn of phosphogenesis accompanied by large perturbations in global carbon cycle, namely the Lomagundi positive carbon excursion.

In this contribution we study the weathering indicators and apply different elemental proxies on the FAR DEEP project rock record obtained from Petchenga and Imandra-Varzuga Greenstone Belt and covering the Archean to Paleoproterozoic period. The paleoweathering surfaces penetrated by FAR DEEP drillholes provide a perfect opportunity to document the influence of an oxic atmosphere on weathering processes.

This study focuses on sections exposing weathered continental crust and terrigenous sediments formed ca 2.3–2.4 Ga ago, just before or at the time of the rise of the oxygen in the atmosphere. The values of Chemical Index of Alteration minus potassium (CIA-K) of weathered mafic volcanics and shale units corrected for evident K-metasomatic alteration and authigenic carbonate minerals show values reaching >90 both in the uppermost parts of the weathered units and in shales indicating strong and deep weathering.

Proxies of Ba/Sr, and La/Lu confirm the acidic weathering and intensive leaching while proxies of V/Cr, and Cu confirm reducing atmospheric conditions.

Intensified weathering during the onset of the Proterozoic and particularly the Lomagundi excursion is evidenced by abundant sandstone-siltstone units deposited in Pechenga and Onega Basin during this time interval that are typically supermature quartz arenites indicating complete destruction of other rock forming minerals that would be achieved only by strong chemical weathering.

Acknowledgments:
This study is financed by PUT1511 "Chemical weathering evidence of palaeoclimate and atmosphere composition during the Proterozoic-Phanerozoic transition".

MIDDLE DEVONIAN CLAYS OF THE LIEPA CLAY DEPOSIT, LATVIA: COMPOSITION, SEDIMENTARY ENVIRONMENT AND DEFORMATION STRUCTURES

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Liepa (Lode) clay deposit is the only Devonian clay site exploited today in Latvia. The commercial bed in the Liepa deposit is represented by alternating fine-grained sandstone, siltstone, and clay layers. These deposits are united in the Lode Formation (Fm), which belongs to upper part of the Gauja Regional Stage (Givetian, Middle Devonian). Sandstone is pink to orange, cross-stratified, in places with current ripples and quite rare tidal structures. Siltstone usually is greenish and bluish grey, with planar lamination and current ripple structure. Clayey siltstones to silty clays of purple, red, and variegated colours are dominant in the Lode Fm. These deposits have either homogeneous structure or have peculiar network of sub-vertical, branched structures, which most possibly are plant roots. Grain-size and sedimentary structures of the sandy to clayey deposits allow to suggest their accumulation in very shallow water – in rapid currents to low-agitation regime.

Yellowish-grey clay is the most fine-grained in the Liepa site. It is present as lenticular bodies, up to 120 m wide and 30 m thick. Their northern margin dips to south in angle of 7–50 degrees, it cuts underlying deposits of the Lode Fm. This clay contains abundant, well-preserved fossil fish remains, invertebrates, plant remains, and other fossils documented in previous studies [1]. Fine-grained clay lenses are supposed as formed as infillings of slump depressions formed on delta slope [2], [3].

There are different opinions on sedimentary environment of deposits of the Lode Fm. V. Kuršs describes their accumulation in delta slope to shallow sea environment. Phosphate concretions rich in cerium and other rare-earth elements indicate the influence of sea-water, but slump depressions filled with clay points to the existence of inclined deltaic slope favourable for mass movements [2]. Very good preservation of fish fossils evidences rapid burial of fish bodies, also pointing to subaqueous slumping processes [4]. A. Pontén and P. Plink-Björklund [5] suggest that the deposits of the Gauja Regional Stage, including the Lode Fm, accumulated on delta plain to delta slope with dominant influence of fluvial currents. This conclusion is based on detailed sedimentological logging and facies analysis [5]. Uncertainties on sedimentary environment of deposits of the Lode Fm still remain, since widespread sedimentary structures indicate very shallow water settings and don't confirm the existence of delta slope, but existence of the lenticular bodies of fine-grained clays points to delta slope environment.

The clayey deposits of the Lode Fm in the Liepa clay pit are deformed also as a result of Pleistocene glacial activity. Vertically lying beds, folds, and calcite veins related to fractured zones in clays indicate the presence of the glacial dislocations. As some deformation structures created by slumps in the Devonian and by glacier much later in the Pleistocene can be quite similar, the interpretation of sedimentary environments and post-sedimentary changes of the deposits of the Lode Fm is complicated and requires future studies.

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THE COMPOSITION AND USEFULNESS PERSPECTIVES OF KATLESI GEOLOGICAL SUITE OF MEDNIEKI DEPOSIT CLAY

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Clay reserves of Katlesi geological suite are remarkable – they are one of the largest in Baltic States, yet relatively little studied [1].

T. Zenchenko [2] feasibility study of Mednieki clay deposit by drilling showed that the depth of clay layer is up to 20 m. M. Stiebrina [3] investigated the deposit by drilling holes up to 6m depth, and clay resources of the deposit were updated. In turn, K. Jurevics [4] researched white burned clay of Mednieki deposit and proved it as suitable for manufacturing qualitative ceramsite.

Thin layer of dolomites was found under the quaternary layer [5] that partially complicates the extraction of clay. But in places where agricultural land has been established dolomite layer has been removed and partially utilized for lime producing.

In this research for the first time detailed phase and composition study of Mednieki deposit clay is being carried out. Clay samples were dried till air-dry state and crushed in powder. Analysis of elements was carried out using XRF method with X-ray Fluorescence spectrometer (XRF) S4PIONEER (by Bruker AXS GmbH). Phase fixation was carried out using XRD method with X-ray Diffractometer D8 ADVANCE (by Bruker AXS GmbH).

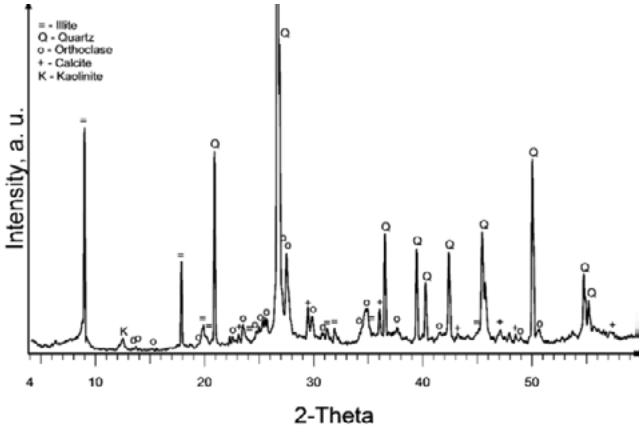

Fig. 1. Mednieki deposit clay X-ray diffractogram.

Study on use of clay from Mednieki deposit for creation of porous light ceramics using lake organogenic sediments has been started.

Acknowledgments:
The authors would like to thank RTU Institute of Inorganic Chemistry for the opportunity to use X-ray diffractometer and spectrometer, and Aija Krūmiņa for consultations.

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COMPREHENSIVE CHARACTERISATION OF BENTONITES FROM CROATIA AND NEIGHBOURING COUNTRIES

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There are several known deposits of bentonites in Croatia. Some of them have been used in the oil and casting industry and were thus studied with the focus on their appropriate properties. In the first comprehensive characterization of the Croatian bentonite deposits [1] mineralogical and petrological characterisation of investigated bentonites was performed leading to conclusions about their genesis. With the advancement of analytical methods and new findings about smectite characterisation in recent years, a demand for a full characterisation of known bentonite deposits occurred.

Thirteen samples of bentonites were studied, most of them from Croatia (Poljanska Luka, Bednja, Draga–Gornja Jelenska, Lončarski Vis, Sjeničak, Paripovac, Divoselo and Bunarić–Maovice), but for comparison, samples from Bosnia and Herzegovina (Šipovo), Slovenia (Zaloška Gorica), and Serbia (Vranjska Banja) were also analysed. Their mineralogical and chemical characteristics were analysed using several analytical methods on whole rock and <2μm samples. Mineralogical composition was determined using XRD and IR analyses. Chemical composition was determined using ICP/AES and ICP/MS. Additionally, thermal analyses have been made, as well as determination of CEC and the exchanged cations. Layer charge was determined both by chemical formulae calculations using chemical analysis data and experimentally, observing the swelling behaviour of potassium saturated samples solvated with ethylene glycol. The results were then compared with the classification system proposed recently [2].

According to this classification scheme, the main mineral component of most of the investigated bentonites is a calcium-rich dioctahedral montmorillonite with experimentally determined low layer-charge deriving from the substitutions mostly occurring in the octahedral sheet with variable share of tetrahedral substitutions. However, three of the investigated samples contain beidellite as the main mineral. All of the bentonites were formed from altered volcanic material, their age ranging from Late Jurassic to Late Miocene. Some samples proved to be difficult to characterise as they contain impurities, both mineralogical impurities and amorphous substances such as volcanic glass, which rendered some of the data obtained by chemical analyses problematic to interpret.

Overall, the results present a systematic classification of local bentonites based on latest analytical data and in accordance with widely accepted classification schemes. Inevitably, however, this work opens up questions about the reliability of some analytical methods when dealing with samples containing impurities and the need to complement several different analytical methods in order to obtain accurate results.

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CLAY MINERALS FROM THE ANTEI-STRELTSOVSKOE URANIUM DEPOSIT (RUSSIA)

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Antei-Streltsovskoe deposit (ASD) is located in Zabaykalsky Krai, Russia in the eastern part of the biggest Russian uranium ore field, called Streltsovskoe (SOF). SOF is confined to a caldera formed in the Late Mesozoic. Then the area of the ASD was subjected to a complex low-temperature metasomatic alteration, which resulted in three stages of mineral formation: pre-ore stage (140–135 Ma), uranium ore stage (135±2 Ma) and the post-ore stage (135–117 Ma) [1].

Mineralogical investigations of the SOF have been started since 1960s. Over the years, numerous data have been accumulated that allowed different researchers to substantiate the schemes of stages and paragenetic sequences of mineral formation. However, in view of the multistage nature and duration of the hydrothermal processes taking place in the SOF, a comparison of those schemes reveals some differences, in particular, for clay minerals. The aim of this research is to study clay minerals from the wall-rock metasomatites, to clarify some disputable aspects of genesis of this deposit.

53 core samples from wells 4 and 7 were selected for the study. These wells pass at depths of 800–2200 m through the late Paleozoic granites of the Streltsovskoe caldera basement [1]. The samples were studied by a series of methods: XRD analysis, quantitative analysis of bulk samples with the Rietveld method and simulation of XRD patterns of textured clay specimens for identification and quantification of mixed-layer minerals, FTIR spectroscopy in the middle infrared region, SEM and EDS. Separation of clay fraction was conducted by sedimentation.

Four associations of clay minerals have been distinguished in the metasomatites of the ASD. The first association consists of illite, mixed-layer illite-smectite with a predominance of illite interlayers. The second association consists of illite with a high content of minerals of the kaolinite-serpentine group (kaolinite, berthierine). The third association is distinguished by the presence of the chlorite group minerals. The fourth association is distinguished by the presence of the smectite group minerals and mixed-layer group of disordered illite-smectites.

The obtained results generally agree and elaborate the research published before [2]. The revealed mineral associations reflect the formation sequence of clay minerals in metasomatites of the ASD: 1) ubiquitous occurrence of illites and illite-rich mixed-layer illite-smectites as a result of hydrothermal processes in the pre-ore stage; 2) formation of the kaolinite-serpentine group minerals (kaolinite, berthierine) under the influence of hydrothermal processes of the post-ore and uranium ore stages accordingly imposed on the mineral association 1; 3) formation of smectite group minerals and mixed-layer disordered illite-smectite minerals under the influence of the latest imposed post-ore (hydrothermal) processes confined to the crush zones.

Acknowledgments:
This study was partially financed by the laboratory budget of project # 0136-2014-0009. XRD study was carried out on the equipment obtained with the funding of Moscow State University Development Program.

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THE SIGNIFICANCE OF CLAYS IN AGRICULTURAL SOILS IN LATVIA

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Soil is one of the key elements in agriculture. Among important soil formation factors are parent materials – the mineral materials from which soil forms, and their transformation processes to the soil. To a large extent they are linked with soil physical texture, which is used for soil classification also in agriculture.

Soil texture is determined by soil mineral particles that are grouped according to their size (sand, silk and clay). Each group is characteristic for important properties, expressed to a different degree, respective to the soil processes (e.g. aeration, drainage, water holding capacity) and interactions with organic world (e.g. decomposition of organic matter, ability to store plant nutrients). The ratio of soil mineral components of different size determines the soil type. Thus, soil type is an important characteristics in agriculture, because it is connected with field crop production.

Clay is one of the four major distinguished textural classes of the soil. In respect to agriculture, despite the fact that it, unlike sandy soil, is able very well to attract and store nutrients that plants need, clay often suffers from bad reputation, because it can be hard to cultivate and it drains very slow. Līpenīte and Kārkliņš [1] in their scientific review and analysis of the importance of soil physical and agrochemical properties emphasized also the specificity of clay soils in the context of land use changes.

There are 1288 thousand ha of arable lands in Latvia [2]. Unfortunately, currently there is no precise information on how soil of this area is divided into grainsize classes, according to the soil classification system in Latvia, presented in Table 1. Such information would be important for developing cultivation technologies for the planning of the non-traditional crop cultivation, which is becoming more and more urgent due to the climate change.

Table 1

Soil Texture Classes According to Latvian Soil Classification System [3]

Granulometry	Proportion of physical clay (<0.01mm), %
Medium and heavy clay	>66
Light clay	65–51
Heavy till loam and heavy silty till loam	50–41
Medium till loam and medium silty till loam	40–31
Light till loam	30–21
Sandy loam and silty sandy loam	20–11
Coherent sand	10–6
Lose sand	<10

In the period from 2013 to 2017 during the weed monitoring in Latvia, 288 fields of farms at Kurzeme, Latgale, Vidzeme and Zemgale regions were included in soil survey that involved also determination of soil texture. The correlations between soil granulometric composition and distribution of weed species, as well as productivity of crops grown in respective fields have been tested. The obtained data in the Vidzeme region indicate that the yield variables have had little influence from the variation of physical clay particles from 31−50 %.

Acknowledgments:
This study was financed by the Ministry of Agriculture grant project "Recommendations for effective control of wild oat and other widespread weed species in Latvia".

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CHARACTERIZATION OF THREE DIFFERENT LATVIAN CLAY MINERALS FROM DIFFERENT GEOLOGICAL PERIODS

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Latvia is a rich in clays country, it has lots of clay deposits containing different clays. Mainly clays are used as a raw material for producing ceramics, building materials, fillers for dyes, etc. As time goes by, clays, especially their nanofractions, have become a raw material for untraditional and more delicate purposes – they are being used in medicine, pharmacy, etc. In this case it is a must to know the structures and properties of these minerals in order to obtain high quality composites. Some clays may be more appropriate for specific goals than others due to their properties; therefore it is very important to carry out investigations to find the most appropriate ones.

Description and characterization of 3 different clay nanosized minerals from 3 different geological periods (Devonian Liepa clay, Triassic Saltiski clay and Quaternary Apriki) are summarized. The main minerals in these clays are illite and kaolinite. Nanosized clay mineral particles were obtained using sedimentation method. Comparison of mineralogical composition, BET nitrogen adsorption, Zeta potential, DTA analysis and FTIR spectra is given.

XRD phase analysis results are very close to each other and show that there is more mineral of illite than that of kaolinite. BET nitrogen adsorbtion data shows that Apriki clay has the highest specific surface area (81 m^2/g), whereas Saltiski clay has the lowest (43 m^2/g). Zeta potential values for Apriki, Liepa and Saltiski clay are –40.9 mV, –49.6 mV and –43.0 mV, respectively. DTA analysis and FTIR spectra show similar tendencies for all 3 clay minerals.

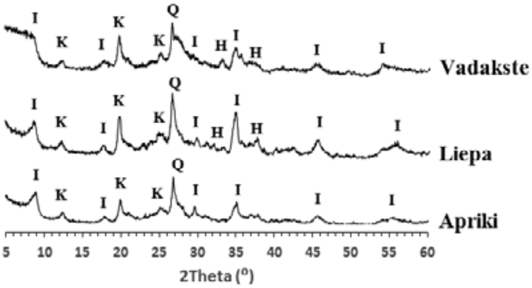

Fig. 1. XRD pattern of used clay minerals: K – kaolinite; Q – quartz; I – illite; H – hematite.

SOIL TILLAGE INFLUENCE ON CLAY MINERAL COMPOSITION AND ORGANIC CARBON ACCUMULATION IN SOIL

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Physical-chemical properties of soils are mostly dependent from clay mineral and grain-size composition and properties of soil organic carbon (SOC) [1]. Whereas soil tillage and crop rotation has short and long term influence on soil system disturbance and promote changes on soil physical and chemical properties [2]–[4]. The actuality of the study is highlighted by increased scientific interest in last decade about SOC stocks, sequestration and possibilities of SOC resources stabilization [5]. The most effective mechanism for SOC stabilization is reducing loss of organic carbon by microbial activities through SOC sorption to mineral surfaces, preferentially on smectite surfaces [5], [6]. For understanding SOC dynamic and stabilization processes good knowledge of soil humus and clay sized materials in soil is required. We studied soil tillage and crop rotation system influence on clay mineral composition and correlation with organic carbon accumulation in soil and agro-physical-mechanical properties.

The study site is located in the southern part of the Middle Latvian lowland Zemgale Plain at monitoring field with different crop rotation and tillage system (conventional and minimal) performed, established since 2009. The studied sod-stagnogley soil is formed on Weichselian loamy to loamy-clayey glaciolacustrine sediments. Soil is rich in carbonates, with pH KCl 6.0–7.3, organic carbon content with seasonal variation in topsoil 1.3–1.9 %. Clay mineral composition characterize illite, kaolinite, chlorite, smectite and illite-smectite. The high mixed-layered clay mineral (MLM) content under topsoil in fields with conventional tillage was identified. The tests of agro-physical properties (volumetric weight, capillary porosity, potentiometric resistance and grain size composition) in long term conventional tillage fields draw tendency on plough pan formation and partly could explain MLM formation under topsoil. The seasonal character of MLM and SOC accumulation correlation with clay mineralogy were not determined and future investigations are necessary.

Acknowledgments:
This study was financed by the Ministry of Agriculture, Republic of Latvia (grant S310 "Reduced soil tillage impact on soil fertility, development and distribution of harmful organisms, yield and their quality in monoculture").

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SESSION: CLAY-BASED COMPOSITE MATERIALS

APPLICATIONS AND LIMITS OF ORGANOCLAYS

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Clay minerals with their large specific surface area, ion exchange capacities and outstanding hydration properties with an exfoliation of the nanosheets that can self-assemble in liquid crystalline phases [1] display particular interests as adsorbent materials, reinforcers in polymer nanocomposites as well as host matrix for the preservation of biomolecules or to confine and orientate guest molecules in hybrid materials.

Surfactants used as chemical modifier to develop hybrid organoclay materials and/or in association with clay mineral in solution generate a hydrophobic environment improving and enlarging the possible applications of raw clay minerals [2]–[3].

In this present contribution, we focus on the preparation of novel organoclays based on nonionic surfactants [4]–[5] and discuss and compare their properties and possible uses to conventional cationic organoclay systems (i.e. prepared with alkylammonium cationic surfactants) and raw clay minerals. Non-ionic organoclays with their dual hydrophilic/hydrophobic behaviours, unlike cationic ones showing a hydrophobic surface, and untreated clay minerals displaying a hydrophilic behaviour, represent the most polyvalent material for the adsorption of a wide range of micropollutants showing different chemical nature but also a hydrophilic behaviour intermediate between the two other adsorbents [6].

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CACL$_2$/BENTONITE COMPOSITE: WATER SORPTION CAPACITY AND KINETICS FOR HEAT STORAGE APPLICATIONS

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In the last decade, clays have been identified as promising materials for dispersing salt hydrates in order to improve the hydration process that can then take part at low water vapour pressure [1].

In this perspective, the aim of the present research is to enhance the heat storage and mass transfer performances of mesoporous materials by adding hygroscopic salt. Bentonite (B) was chosen as supports of 15 wt% of calcium chloride (Ca_{15}) and the obtained composite was compared to those prepared on more conventional mesoporous supports as silica-gel (S) and alumina (Al). The comparison between the three series of composites (BCa_{15}, SCa_{15}, $AlCa_{15}$) was done by analysing the impact of the salt addition on the physico-chemical and sorption properties of the three host matrixes. Moreover, the water sorption/desorption kinetics on the different composites under operating conditions, close to those of heat pump

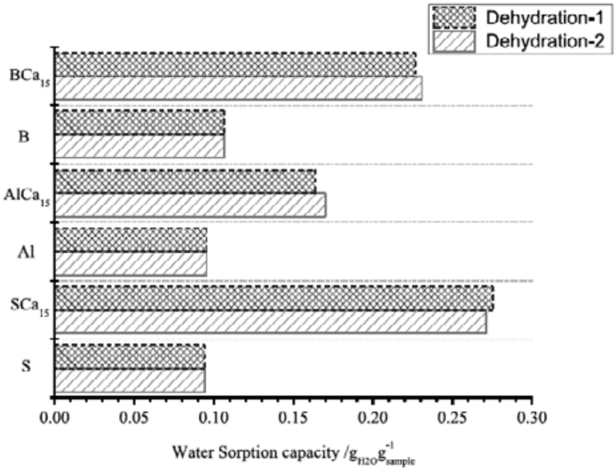

Fig. 1. Water sorption capacity of supports and composites.

application, has been studied. The thermal behaviour of the composite materials was examined by TG/DSC analysis [2].

The addition of calcium chloride increased the quantity of sorbed water and released heat.

Finally, the experimental results of rehydration were fitted with kinetics model in order to describe the kinetics of water vapor adsorption of the three mesoporous composites.

Despite the smaller surface area, bare bentonite adsorbed more water than silica and alumina at relative humidity of 30 % (see Fig. 1). This behaviour is most likely linked to the non-rigid structure of bentonite which can host huge quantities of water by swelling out. Among the supports, bentonite showed the highest value of dehydration heat (61 $kJ.mol^{-1}{}_{H2O}$ and 356 $J.g^{-1}{}_{sample}$). In bentonite, water molecules can indeed diffuse between the structure layers forming hydrogen bonds with the hydroxyl groups of the clay structure, thus providing higher heat values.

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GAS CHROMATOGRAPHY AS A POWERFUL TOOL TO STUDY THE SURFACE PROPERTIES OF SYNTHETIC AND MODIFIED PHYLLOSILICATES AS WELL AS OF MODIFIED PHYLLOSILICATE/POLYMER COMPOSITES

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Inverse Gas Chromatography (IGC) enables gathering information on the interaction potential and physicochemical properties of materials. Measurements are performed by injecting chosen and known molecules, called molecular probes, in order to get chromatograms. The retention times, as well as the shape of the obtained peaks, are depending on the interactions occurring between the molecular probes and the investigated material (stationary phase). The multiplicity of the used molecular probes allows a complete description of the interaction potential of the material with the fast determination of numerous surface characteristics like the surface energy (γ_s^d), the surface nanoroughness, the acid-base character and the surface morphology. Beside conventional characterization techniques (X-Ray diffraction (XRD), solid state nuclear magnetic resonance (NMR) spectroscopy…) IGC can therefore shed light on the influence of the treatments (ion exchange, grafting, …) on the surface properties.

In this work a series of clays (natural and synthetic Na-montmorillonites, synthetic Na-beidellite), hexadecyltrimethylammonium ($C_{16}TMA^+$) and octadecyltrimethylammonium ($C_{18}TMA^+$) treated clays as well as a polymer/C_{16}TMA-beidellite nanocomposites were characterized by IGC as well as by XRD, thermal analysis and solid state NMR (^{19}F, ^{13}C).

It was shown that there are very strong polar interactions on the natural Na-montmorillonite, as well as on the synthetic Na-beidellite and Na-montmorillonite. It is worthy to note that the dispersive component of the surface energy (γ_s^d) decreases strongly after organic treatment, whatever the clay, meaning a lowering of the surface interactivity. The determination of the morphology indices indicates also a decrease of the surface roughness. The value of γ_s^d of the neat polymer and C_{16}TMA-beidellite polymer nanocomposite are similar indicating that the polymer covers totally the clay particles.

WOOD AND INORGANIC GEOPOLYMER COMPOSITE

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Along with the development of ecological and environmentally friendly architecture the wood has become an irreplaceable element in the concept of green building. One of the disadvantages of wood is its low fire resistance, which requires searching for effective solutions to prevent it. At the same time, geopolymer is an alternative material of concrete with lower CO2 emissions. This paper looks at wood-geopolymer composite as one of the possible solutions to combine these two environmentally friendly materials.

The first part of research describes softwood – pine (Pinus sylvestris L.), spruce (Picea abies [L.] Karst.), and hardwood – birch (Betula pendula Roth), binding with inorganic geopolymer binder, the main focus is on the hardwood and geopolymer binding principles. Geopolymer binder is formed from calcined clay and liquid glass. The research describes geopolymer binder compositions with various content proportions of liquid glass and minerals. This research focuses on mechanical strength of bonded wood samples in shear test and on visualization of binder in three dimensions using X-ray computed tomography with submicron resolution. The results of the research show, that inorganic binder with birch wood can achieve 7 MPa shear strength. The research describes binding principles that function between wood and geopolymer and explains the main reasons for destruction of joint. Further parts of research describe wood geopolymer properties. In this case the geopolymer is formed from clay, which is mined in Latvia (silico-aluminate), and water glass (silico-oxide). The wood-geopolymer was made by mixing geopolymer with softwood particles. The aim of the research was to develop a wood-geopolymer composite material and to evaluate their optimal composition and properties. The study defined the impact of the compound for mechanical and physical properties (bending strength, compressive strength, modulus of elasticity, swelling and thermal conductivity) of wood-geopolymer composite. The current paper presents mechanical properties of different composition and treatment method of wood-geopolymer. As a part of the research the geopolymer and wood geopolymer thermal conductivity were compared. Results have shown that there is a correlation between wood-geopolymer density and thermal conductivity. The same correlation was observed between wood-geopolymer density and mechanical strength. [1]

This is an overview of the wider study on the use of wood and geopolymer composites for the development of heated/cooled wall panels.

Acknowledgments:
This study was supported by the European Union Seventh Framework Programme FP7 under Trees4Future project (grant agreement No. 284181).
The authors express their thanks to the National Research Programme Forest and Earth Entrails Resources: Research and Sustainable Utilization – New Products and Technologies (ResProd) 2014–2017 for financial support.

RESPROD

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OPTIMIZATION OF CARBON FIBRES COVERAGE BY A THIN LAYER OF ORGANOCLAY CONTAINING IRON

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The synthesis of a carbon/organoclay composite is a simple one-step sol-gel procedure that allows direct contact between the carbon fibres and the clay solution (aminoclay solution) [1]. After the material is obtained, both the aminoclay alone and the aminoclay that was in contact with the carbon fibres are characterized using different techniques such as XRD, XRF, FTIR, TGA, and solid state NMR. On the impregnated carbon fibres, SEM and EDX analysis were performed in order to observe the homogeneity of the aminoclay layer.

The analysis carried on the aminoclay showed that a talc-like structure is obtained with XRD peaks, FTIR bands, TGA curves, and NMR resonances in good agreements with data from the literature. Moreover, it was evidenced that the aminoclay is also formed in the presence of carbon fibres. However there were still some differences observed between the pure aminoclay and the composite material: for example, the presence of the iron oxides was observed for the aminoclay prepared without magnesium source whereas no side phase was observed with the composite sample. The synthesized composites prepared starting from aminoclays solutions containing different wt % of metallic compounds were also characterized by SEM in order to observe their morphology. Another feature to observe in the SEM analysis was the influence of the order of addition between the material and the organic part. It was observed that both the metallic content and the addition order influence the coverage of the carbon fibres by the aminoclay.

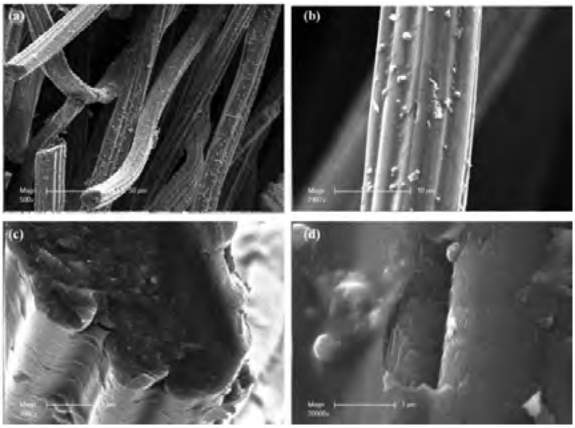

Fig. 1. SEM image corresponding to a carbon/aminoclay composite containing 100 wt% of Fe in the octoedral sheet.

Acknowledgments:
This study was funded by the Institute of Science of Materials of Mulhouse in the frame of "call to emerging project" and performed in collaboration with the Institute of Chemical Sciences of Rennes.

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HECTORITE AND BENTONITE EFFECT ON WATER-BASED POLYMER COATING RHEOLOGY

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Increased interest in aesthetic, natural nail coatings has encouraged more in-depth studies, and particularly of UV curable coatings: their formation, processing, characteristics and removing. This study investigated the impact of various thixotropic agents (hectorite and bentonite clays) on water based oligomer system rheology. Ingredients were evaluated to determine their influence on unreacted composite characteristics (viscosity, flow ability, suspension pigment stability) and reacted film characteristics (ultimate strength, elongation at break, surface gloss, film adhesion force, and coating removability). It is concluded that thixotropic agents are suitable for use as a suspension agent in nail polish formulations and depending on the concentration can decrease the risk of pigment sedimentation and syneresis.

Acknowledgments:
This research was supported by CFLA project No. 1.2.1.1/16/A/006 "Effect of Silicate rheology modifiers on solvent based nail coating syneresis and sedimentation".

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FUNCTIONALIZING NATURAL STRUCTURES BY ILLITE NANOPARTICLE DEPOSITION

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In recent years many studies of clays are focused on clay minerals as natural nanoparticles [1]. Illite nanoparticles can be used in the development of high-performance products such as modified cellulose with improved thermal properties [2]. It may be possible to use illite in combination with other natural materials to produce new and innovative materials, however studies in this particular direction are very few.

This study investigates the possibility of producing biomorphic ceramics by depositing illite nanoparticles on natural material templates.

Natural templates used in this study are wood, moss, lichen and cotton fiber. Source of illite is quartenary clays from the Apriķi deposit in western Latvia. Deposition of illite nanoparticles was done by immersing templates in water-illite slurries for 1 to 24 hours. After drying samples were sintered in air and nitrogen at 800 °C to 1000 °C.

Morphology of sintered samples was analysed using SEM (model NovaNano SEM 650) and phase composition by XRD (model D8 Advance Bruker and model Rigaku, Japan with CuKα radiation at 2θ scanning interval from 10° to 60° and speed 4°/min.).

Sintered biomorphic ceramics does retain macroscopic features of the moss and lichen templates. Microscopic morphology so far is retained only in one sample – lichen template sintered in air at 1000 °C. XRD shows weak peak intensities due to glassy structure of samples. Main phases in sintered samples are anorthite, quartz and hematite (in air) or iron (in nitrogen). All samples are very heterogenous and have low mechanical strength, which greatly diminishes their practical application.

For practical application technology must be significantly improved to increase homogeneity and mechanical properties. Such material then could be used as thermal insulator, filter material or as sorbent.

Acknowledgments:
This study was financed by project 1.1.1.1/16/A/077 "Mineral and synthetic nanopowders for obtaining porous ceramics and modification of ceramic materials".

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PROPERTIES AND APPLICATIONS OF CLAY MINERALS MODIFIED WITH DIFFERENT ORGANIC/INORGANIC SUBSTANCES

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Clay minerals have attracted great interest because of their abundance and unique physicochemical properties such as high sorption and ion-exchange capacity. Clay mineral modification using different approaches can deliver innovative materials for wide variety of applications, e.g., water and wastewater treatment, biomedicine, food and biopharmaceutical industries [1].

The research aims to prepare composite materials based on clay minerals and organic molecules or inorganic compounds to evaluate their potential applications in environmentally friendly technologies or bioeconomy. In this study, ionic liquids with different alkyl chain lengths and anthocyanins from the *Aronia melanocarpa L.* berries were selected as the organic molecules while iron oxy-hydroxide as the inorganic compound for modification of natural and synthetic clays dominated by smectite. Clay composite materials were characterised by several physicochemical techniques including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM).

The obtained results indicated that intercalation of anthocyanins into the galleries of the clay minerals stabilized them, therefore it can be concluded that composite materials can be used, for example, as natural colorants in the food industry or as enterosorbents. Modification of clay minerals with iron compounds and various ionic liquids significantly improves sorption capacity and newly developed materials can serve as sorbents for the removal of inorganic and organic pollutants from aqueous solutions.

Acknowledgments:
This study was financed by the Latvian State Research program *Res Prod* project No. 2014.10-4/VPP-6/6, the European Regional Development Fund within the project No. 1.1.1.1/16/A/047 "Genus Vaccinium berry processing using "green" technologies and innovative, pharmacologically characterized biopharmaceutical products", Interreg South Baltic project "Reviving Baltic Resilience" (RBR) and Geo IT Ltd.

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PRODUCTION AND PROPERTIES OF LOW-TEMPERATURE GLASS-CERAMIC FOAM BASED ON ILLIE LATVIAN CLAY

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Environment, energy, health and transport issues are dominating our modern daily life. The complex interactions of these problems can only be solved by sustainable processing and development of improved porous components. Clay is one of the most available and cheap natural resources, which can be used for the production of construction and insulation materials. Several papers describe the production of porous components based on geopolymers made by direct foaming, thus typically following approaches similar to those employed in the cement industry (i.e. in situ generation of gas [1], [2]), leading to the creation of mainly closed cell foams. The method of foaming by gas forming in the process of reaction, e.g. oxygen, is known as well [3]. Biological foaming technique through reaction of yeast with starch in aqueous ceramic suspension was studied as well [4].

Wastewater purification from organic contaminant and reuse of secondary materials are current issues in agriculture and industry. Reuse of waste glass (WG) for production by low-temperature clay ceramic foam in SCOPE for the Baltic region, rich with clay deposits, and EU circular economy policy is of particular importance. Open cell structure of the clay-WG ceramic foam (CCF) could successfully be used as filter for water purification. The CCF were produced with different WG content 5, 7, and 10 wt% by direct foaming technique and subsequent sintering at 900, 950, 1000 and 1050 °C. The removal of *Bezaktiv Turquise Blue V-G* dye from aqueous solutions by CCF was studied through batch adsorption experiments.

The effects of pH of solution, contact time and equilibrium isotherm parameters onto the adsorption process were investigated. It was proved that the CCF samples were effective in removing dye from aqueous solutions, being the most effective, as far as its maximum adsorption capacity was obtained at pH = 2 (below point of zero charge), to be 1.7 mg/g. The time required to reach the equilibrium between the solid and liquid phases was 300 min. The kinetics studies showed that the experimental data were well fitted by the pseudo-second-order model with (R^2 = 0.91 – 0.99). The isotherm experimental data were a better fit to the Langmuir model, showing a maximum monolayer adsorption capacity of 8.80 $mg.g^{-1}$. Owing to the relatively simple clay foam production technology of using direct foaming method and cheap and readily available raw materials, CCF is promising for water treatment.

Acknowledgments:
This research was financially supported by the Latvian National Research Program "Studies of mineral resources – the new products and technologies" (Earth) 2nd subproject.

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SESSION: CLAYS IN ARCHAEOLOGY AND ARTS

IRON COMPOUNDS IN THE POTTERY: TEMPER OR COINCIDENCE? A CASE STUDY OF KRIEVU KALNS HILLFORT

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The aim of this paper is to find out if iron compound (iron hydroxide group) lumps in Krievu kalns hillfort pottery matrix could be a temper or just a coincidence. To reach this aim, the author has macroscopically analysed all the sherds of Krievu kalns hillfort which contains iron compound lumps. Also from one striated pottery sherd a thin section was made to petrographically analyse it. The thin section was analysed by Ole Stilborg (*Stilborg Keramikanalys*) in February 2015.

12 percent of all sherds from Krievu kalns contain iron hydroxide lumps. Iron compound lumps mostly occur in striated pottery. They have various forms, mostly oval-shaped, elongate and bumpy. Iron compound hardness depends on its colour – light red is fragile, but dark brown and liver-coloured is quite hard.

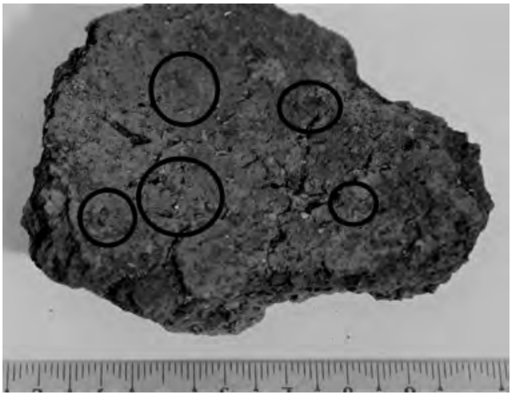

Fig. 1. Small light brown iron compounds in pottery
(LNVM, collection of Krievu kalns pottery, Inv. No. A13957:38, photo by V. Visocka).

All sherds, which contain iron hydroxide lumps, also contain granite temper. The most common size ratio between iron compound lumps and granite is 2–4 mm against 2–4 mm. Some sherds contain quite big iron compound lumps in matrix, up to 8 mm in diameter. Petrographic analyses showed that striated pottery sample was made from medium coarse clay which is rich in mica and oval-shaped iron hydroxide lumps (max grain size is 3.9 mm), granite is used as a temper (it contains 15–17 percent in clay), clay also contains iron ore. O. Stilborg does not view iron hydroxide lumps as temper in clay, it has formed from naturally occurred iron in clay. The determination is based on the rounded form, the un-solid character integrating with the clay matrix and the presence of iron lumps in all sizes.

Comparing the nature of iron compound lumps from Krievu kalns and other sites (Ķente [1] and Asote [2] hillforts and Tērvete site [3]) a lot of similarities were detected – the colour (light red, dark brown and liver-coloured), appearance, forms (oval-shaped, bumpy) and size (up to 8 mm). These similarities, as well as the size of iron compound lumps makes the author think that it could be a tempering tradition.

To make more assumptions about iron lump inclusions in pottery matrix, further research needs to be made (petrographic and X-ray fluorescence analysis).

Acknowledgments:
Author would like to thank O. Stilborg for making petrographic analysis.

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REHYDROXYLATION METHOD ADOPTION EFFORT ON DIFFERENT AGED CERAMICS FROM LATVIA

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Rehydroxylation (RHX) method is a rather new absolute dating method for fired clay-ceramics [1]. The method relies on the ceramic material properties that determine immediate recombination chemically with moisture from the environment after the firing. It is a two-step process of rehydration (I stage) and rehydroxylation (II stage). According to the method the reaction of the ceramic object with water vapour can be observed after reheating of the sample (in a high temperature) and further exposing it in stable conditions with relative humidity and temperature (similar to the sample average life time conditions). The stage I process is comparatively fast and corresponds to the absorption of water molecules through the surface into the open porous system of the ceramics. In the following stage II, that is much slower, the hydroxyl water is incorporated into the clay minerals and ceramic object undergoes the rehydroxylation process, which follows the (time) 1/4 kinetic law [2]. Before the reheating of the sample the initial mass is determined and it reflects the mass of the sample after firing and mass of the water bonded to the structure during deposition and conservation. After the reheating the mass of the sample regularly is determined with a high precision. By extrapolating the data of mass gain during stage II according (time) 1/4 kinetic law, it is possible to calculate the estimated age of a ceramic sample. The method is self-calibrating and it is important to follow certain procedure for obtaining comparable data. The results are dependant from applied methodology (e.g., reheating temperature, stable conditions mode) as well as from the studied material itself (e.g., mineralogical composition, firing temperature, deposition history). So far the studies show promising results, but further investigation about factors influencing data and more testing on real samples are needed [3].

In our study we tested 22 ceramic samples from Latvia. They refer to different prehistoric (5400–1800 B.C.) and historic (2–9th century, 12–13th century, 17th century) periods, as well as include modern bricks samples (2005, 2013). Accordingly, their deposition and conservation conditions have been different. Sample sizes ranged from around 670–2700 mg and they were tested in two different research modes. Part of the samples were fired in 500 °C and the mass was determined each 12 h for 14 days. Other part was fired in 700 °C and the mass was determined each 24 h for 7 days. The stable experimental condition was 4.8 °C with relative humidity 90 %. We did extrapolation of the stage II data according (time) 1/4 power law.

The first results indicate that it is possible to distinguish modern samples from the historic and prehistoric samples. The precision of the results is variable and requires further studies regarding influence factors. The results on prehistoric and historic samples indicate unacceptable uncertainties for dating and require further studies.

Acknowledgments:
Special thanks to colleagues B. Dumpe, A. Skulte and J. Ciglis from the Department of Archaeology of the National History Museum of Latvia for the given ceramics collection.

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CLAY MATERIALITY AND PROCESSES HAPPENING TO IT AS ARTISTIC RESEARCH

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The core of my artistic research is material with its properties and processes as well as objects/artefacts resulting from them. We can see those artefacts as the means for storing information, understanding it, as the methods of preservation and convention in the frame of artistic research.

I explore the material and its processes through the prism of "maker/thinker". In my artistic research I tend to connect these two perspectives, which seem opposite at the first glance. The material (clay) is being explored in two ways: using the sense of tactility, following and responding to its properties and processes as well as intellectually, forming new conceptions, which possibly will result in material. "Making" and "thinking" affects each other both ways.

This research follows ceramic transformations – from material (earth/clay) to the fired object.

Moreover, my artistic research is very much based on two fundamentals – walking and making. Walking is a natural pace to move from one place to another in the natural world and its speed allows for contemplation, reflection and knowledge of the place around. And not only that, walking for me means research as a path of thought. Walking through my internal landscape, gaining new ideas, thoughts and perceptions as well as possibly making new understandings.

As for the making part, I am very much interested in materials and processes, especially in ceramic making. Both traditional and non-traditional. The material itself has so much to offer and all the different processes involved in making it are so complicated that for an eye of non-maker it is an uncovered secret.

I look at the ceramic practice as a method that engages the maker at multiple levels simultaneously. Time is one aspect of the practice that makes a strong connection to the material processes. Every step of the process takes its own time. I intend to link processes of making with perceptions of environmental phenomena, as time here is also fundamental.

The mundane pursuit of walking is an impulse to the generation of thought, in much the same way that the activity of making and manipulating materials through art making may provoke ideas. The physical, bodily connections with the material along with the senses of touch, sight and hearing, are well employed in not only expressing, but also gaining new ideas and assist the processes of thought itself.

Walking is not the subject of my research, but it is a crucial part of it. Clay materiality and processes happening with it, is the subject, and through it I aim to give for those approaching my works a different view of ceramic material and processes involved in the making.

GEOCHEMICAL LINK BETWEEN BUILDING CERAMICS AND ITS RAW MATERIAL: FROM THE 16TH CENTURY UNTIL NOWADAYS. CASE STUDY OF VILNIUS, LITHUANIA

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Revealing of the links between building ceramics production and potential sources of raw clay material and identification of the latter ones is an important task of urban construction archaeological research. Application of geochemical research methods for comparison of building ceramics and raw clay composition is one of the possible ways to do this. Geochemical investigations are understood as a complex of methods which includes: a) purposeful selection of fragment samples of building ceramics finds; b) multi-elemental method of determination of total contents of chemical elements (not less than 20–25 chemical elements including all major elements); c) multivariate statistical analysis (e. g., cluster, factor analysis); d) analysis of the geochemical indices expressed as ratios of elements, reflecting clay and other additives which compose building ceramics; e) graphical representation of results. Aiming to obtain more precise interpretation of origin and technological processes of building ceramics according to geochemical research data, it would be useful to ensure the conditions which were mentioned earlier [1].

Forty archaeological finds from six building ceramics workshops of the Vilnius city were selected as the object of this research. The finds are dated to the 16th, 17th and 18th–19th centuries. Bricks, tiles and floor tiles were manufactured in these brick-yards. In search of their possible raw material sources, clay samples from six geological clay deposits located in the Old town of Vilnius were taken for comparison of their chemical composition with respective composition of archaeological finds. In some brick-yards, not only fired bricks were taken, but also clay mass prepared for firing as well as clay from extraction pits and simply raw clay. Energy-dispersive X-ray fluorescence (EDXRF) was used for determination of chemical composition. The advantage of this method is that great number of chemical elements (>25) can be determined including all those related to clay minerals and their additives (Al, Ca, Fe, Mg, Na, K, Si, Ti) accompanied by specific trace elements (Br, Ga, Cl, Co, Cr, Cu, Mn, Nb, Ni, Rb, Sr, S, P, Zn, Pb, etc.).

For comparison with archaeological production of the ancient Vilnius brick-yards, bricks from two currently working ceramic factories and clay samples from their raw material were selected. These clay deposits were formed during the East and South Lithuanian phase of the Baltija stadial of the Nemunas (Weichselian) Glaciation. Their geological age and mineral composition is similar to the clay deposits in the surroundings of Vilnius, which were possibly used for manufacturing of ancient building ceramics. Chemical composition of samples from modern bricks and clay deposits was determined using analogous geochemical methods (the same sample preparation procedure and the same EDXRF equipment Spectro Xepos, produced in Germany).

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FIRST LITHUANIAN STEPS INTO APPLYING DACTILOSCOPY IN ARCHAEOLOGY

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Klaipėda city (Memel), which is situated on the southeast coast of the Baltic Sea and the Curonian Lagoon, was founded in 1252 as a result of the invasion of the Teutonic Knights to the pagan territory. The documents for its foundation were signed when the castle was built, and throughout several centuries the German culture had been influencing the development of the town, the local way of life, trades and various crafts. Archaeological findings from that region reveal that Klaipėda was a trading and culture exchange centre. This resulted in development of various crafts, e.g., ceramic stove tiles production. An old tradition of heating the house by stoves, which used to be an innovative method in the medieval period, was adopted in Klaipėda as well as in many other European towns.

During the period from 1968 up to nowadays archaeologists have collected over 10,000 samples of stove tiles and their remains in the territory of the castle and the old city of Klaipėda. A lot of studies have been carried out focusing on the decoration and typological aspects of the tiles. The very process of production, however, has been frequently out of the archaeological interest and not studied well enough. The forensic method of dactiloscopic identification may trace back to the past, broaden our mind and shade the light on the history of stove tile production.

As a matter of fact, only in several rare cases the method of dactiloscopic identification has been used in Lithuanian archaeological studies. We suggest that this method can be applied in the study of ceramic stove tiles due to finger imprints which had been left by the craftsmen. In the process of tile production the craftsmen used elastic clay and their finger imprints accidentally or deliberately left on the surface could be found: when they were making holes on sides of tiles or forming an edge of a tile. A dactiloscopic identification of finger imprints on the ceramic stove tiles could reveal which tiles were made by one or another producer. The study could also have an impact on a more detailed chronology of stove tile production and on setting the level of crafting at that time in general.

SESSION: DIFFUSION, SORPTION AND CATION EXCHANGE PROCESSES INVOLVING CLAY MINERALS

ANISOTROPIC FEATURES OF WATER MOBILITY IN SWELLING CLAY POROUS MEDIA AT MESOSCOPIC SCALE

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The anisotropic properties of water migration in natural systems containing swelling clay minerals (smectite or vermiculite) is most often driven by (1) the bidimensional diffusion in interlayer space of the particles and (2) the mutual arrangements of these lamellar particles in the porous media, which induce additional pathways for water transfer.

At the crystal scale, combination of experimental diffraction/scattering techniques and molecular simulations can be used to unravel the details in the organizational and dynamical properties of the fluid confined in the interlayers of swelling clay minerals [1]–[2]. In addition, such a collation procedure provides key quantitative information about the validity of the semi-empirical atomic interaction parameters used in theoretical simulations.

In order to connect the diffusion of water obtained at the scale of the interlayer nanopore with macroscopic property of diffusion, representative porous media for swelling clay minerals are crucial. For montmorillonite, the determination of particle morphology is delicate due to its osmotic crystal swelling in water saturated conditions. To tackle this problem, our efforts have focused in the experimental characterization of swelling clay porous media composed of vermiculite minerals which display similar particle size and shape once immersed in water [3]–[4]. An algorithm, similar to the one proposed by Coelho et al. [5], was used to mimic the three-dimensional organization of swelling porous media for particles having elliptic disk morphology [6]. The obtained virtual porous media are used to perform Brownian Dynamics simulations. Based on the consideration of water diffusion in both interlayer and inter-particle porosity, the obtained results are found to be in fair agreement with experimental data. This allows getting additional insights onto the role played by particle organization on the overall macroscopic diffusion of water.

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STUDIES OF THE LIEPA CLAYS SORBTION PROPERTIES WITH TRITIUM WATER

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Latvian natural clay deposits, such as the Liepa clay, contain illite as main fraction with additions of kaolinite and SiO_2. Illite clay is used for the cation sorption from freshwater [1] and it is a perspective material for sorption of radionuclides from radioactive waste [2].

Study of the Liepa clay is performed to expand the knowledge about Latvian clay application in relation with the isotope sorption and desorption.

Liepa clays (Devon clay, SiO_2 free, grain diameter <2 μm, held in tritiated water (~70 kBq/mL)) were studied. Grains with diameter of <2 μm were chosen, due to the large specific surface area.

Tritium desorption analysis was performed with a coupled system – thermogravimetry/differential thermal analysis (TG/DTA) device together with Fourier transformation infrared spectrometer (FT-IR). The tritiated water desorbed during thermodesorbtion, at TG/DTA device up to 1000 °C analysis, was collected in two Drechsel type gas washing bottles filled with 10 mL deionized water and subsequently analysed by liquid scintillation method.

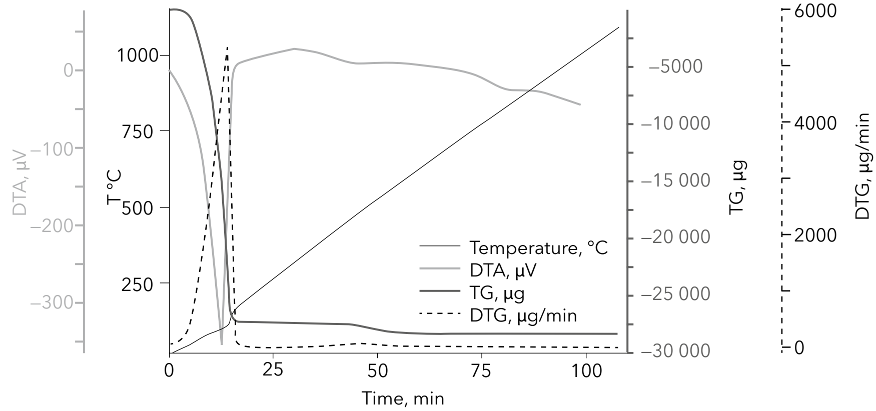

Fig. 1. TG/DTA spectrum of the Liepa clay without tritium water.

The TG/DTA curve analysis shows four main mass loss steps, but in the FT-IR spectra analysis one can see increase of water peak intensity corresponding to the mass loss. The mass loss processes correspond to desorption of differently bonded sorbed water.

In the FT-IR spectra the HTO bonds are at 1332, 2300, 3717 and T_2O bonds at 995, 2237, 2367 cm^{-1} [3]. Presence of such bonds in the FT-IR spectra characterize the tritium sorption/desorption from the Liepa clay grains.

Acknowledgments:
The work is performed in the frames of the University of Latvia financed project No. Y9-B044-ZF-N-300, "Nano, Quantum Technologies, and Innovative Materials for Economics"

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SYNTHETIC CLAYS FOR STUDY OF COMPLEX SOIL PHENOMENA: CASE OF CAESIUM DESORPTION PROCESS

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Clay minerals in soil possess a wide distribution of particle size, different chemical composition, and are submitted to different environmental conditions. Moreover, they are often associated with other mineral phases, which make the interpretation of sorption data particularly challenging. Our group has chosen to work with specifically prepared natural or synthetic samples to overcome these challenges and gain an understanding, how every of these parameters separately have an impact on cesium desorption from swelling clay minerals.

In this study we focus on the influence of layer charge on the fixation of cesium in synthetic smectite. A series of synthetic saponites $^{inter}[Cs_x]^{oct}[Mg_6]^{tet}[Si_{8-x}Al_x]O_{20}(OH)_4$ with layer charge x varying from 0.8 to 2.0 were used [1]. The use of synthetic clay minerals allows working with samples whose crystal chemistry is much more controlled than that of natural clay minerals. Their layer charge is well-defined and covers a range from low to high-charge swelling clay minerals.

The Cs^+ extractability measurements with 1 mol·L^{-1} CH_3COONH_4 showed that the fraction of exchangeable Cs^+ decreased gradually for samples with a layer charge $x \geq 1.4/O_{20}(OH)_4$. The results were found to qualitatively agree with analysis of the thermodynamics of the clay/water interfaces derived from molecular simulations. Quantitative structure analysis by modelling of XRD 00ℓ reflections revealed that the amount of exchangeable Cs^+ can be correlated with the amount of hydrated layers, whereas fixed Cs^+ in these conditions corresponds to the amount of collapsed layers (zero water layers in the interlayer). To describe the coexistence of both exchangeable and fixed Cs^+, a toy model accounting for the presence of heterogeneous charge distribution was used [2]. This model successfully interprets the overall reactivity of Cs^+ toward smectite over a large range of layer charge values and may contribute to an improved description of Cs^+ mobility in contaminated soil environments.

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SORPTION CHARACTERISTICS OF CS(I) AND SR(II) ON BENTONITES

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Bentonites and bentonite-based materials are well known for their adsorption and insulation properties and are therefore widely used to ensure safety in the disposal of various industrial wastes, including those for the disposal of nuclear waste. The main component of bentonite clays, which determines their properties – montmorillonite – is mineral of the smectite group. Its characteristic feature is the ability for intracrystalline swelling due to the lability of the interlayer space, as well as the large specific surface area and high cation exchange capacity.

This work has been conducted on four samples from the deposits in Taganskoye (Kazakhstan), Dashkovskoe (Moscow region, Russia), Zyryanskoe (Kurgan, Russia) and 10th Khutor (Rep. Khakassia, Russian Federation). Composition of the samples was studied by X-ray diffraction, IR spectroscopy, and X-ray fluorescence chemical analysis.

To estimate the adsorption properties, the values of the cation exchange capacity (ECO) were determined by the cationic dye methylene blue (MB) titration method. Experiments on the adsorption of Cs^+ and Sr^{2+} were carried out at static conditions. Thus a series of $CsNO_3$ and $SrCl_2$ solutions was prepared in the concentration range from 50 to 2700 mg/l and from 10 to 1500 mg/l. Solutions were poured into the flasks with bentonite samples at a solid: liquid ratio 1:100. After reaching equilibrium, the supernatants were filtered. Determination of cation concentrations in equilibrium solutions was carried out by ICP-MS. Based on the data obtained, adsorption isotherms were plotted. The shape of the isotherms corresponds to the Langmuir theory, which made it possible to obtain adsorption constants from the linear form of the Langmuir adsorption equation.

The results are given in Table 1. The Tagansky bentonite sample has the highest sorption ability with respect to cesium cations, while the samples of the other deposits have approximately half the values.

Table 1

Adsorption properties of bentonite samples

Sample	Maximum adsorption A∞, meq/100 g		Cation exchange capacity, meq/100 g
	Cs^+	Sr^{2+}	
Taganskoye	104	120	92
Dashkovskoe	58	63	53
10th Khutor	61	80	58
Zyryanskoe	51	81	59

Acknowledgments:
This work was financed by the Russian Science Foundation (Project #16-17-10270). We are grateful to "Bentonite" company for providing us with bentonite samples. XRD study was carried out on the equipment obtained with the funding of the Moscow State University Development Program.

MASS TRANSFER MODELLING IN CLAY-BASED MATERIAL: APPARENT DIFFUSIVITY ESTIMATION OF A MOLECULE OF INTEREST

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The major aim of this work is to develop a numerical model to simulate mass transfer of a molecule in different materials. The studied materials are spherical organic particles, coated or not by a thin layer of clay. They are used to adsorb the molecule of interest and to control the release. For this purpose the molecule adsorption is carried out for both coated and uncoated porous organic material.

The amount of adsorbed molecules is deduced from mass balance before and after experiments. The adsorbent (50 mg) is immersed in 100 mL of pure water (or a 5 mM NaCl-water solution) in a beaker under agitation. Samples are taken for analysis and returned in the beaker.

The thickness of the layer is calculated by clay mass balance during synthesis and was estimated to 2.2 μm (spherical particles, even thickness). SEM investigations revealed a relatively uniform layer of clay (around 2 μm).

From the experimental kinetic curves, the characteristic time of diffusion in pure water can be estimated: $t_d < 7$ hours for the organic material and around 90 hours for the coated material. In the saline solution, the diffusion time is unchanged for the organic material, but increases to more than 300 hours for the coated one. The thick layer of clay has a reducing function of molecule transfer, thus controlling the release. Additionally, the transfer is even more limited in saline solution (only for the clay-based material).

To simulate mass transfer in these materials, differential mass balance is solved in the organic material and in the clay layer to calculate concentration of the molecule. Two boundary conditions are used: a mass flux conservation at the clay/organic material interface and the equality of the amount of the molecules released in water and the molecules outflow from the particles.

According to experimental kinetics of molecule releasing, the mass transfer coefficient (Fig. 1) can be estimated (significant variable in the second boundary condition).

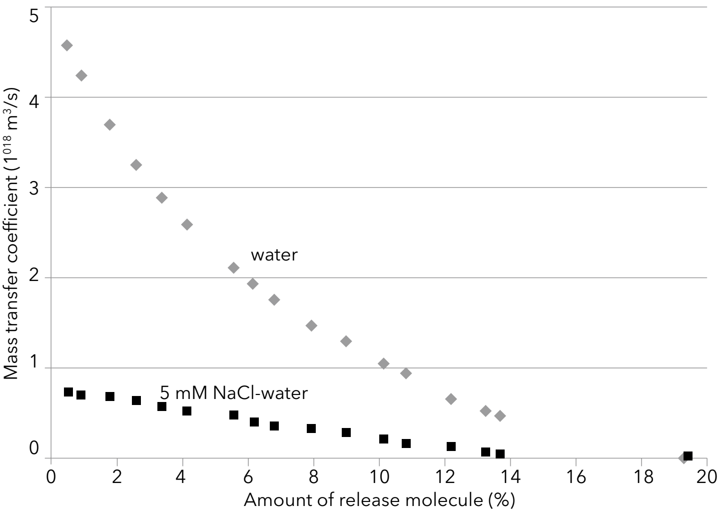

Fig. 1. Mass transfer coefficient (interface water/clay-based material) vs. the amount of released molecule.

The adjustable parameters of the mathematical model (diffusion coefficient of the molecule in the different materials) are estimated by approximating experimental and numerical results. The molecule diffusivity in the organic material is around $6*10^{-13}$ m²/s which is ten thousand times smaller in the clay in pure water and becomes $5*10^{-18}$ m²/s in salt-water solution. As expected, the clay layer ensures the control release of the studied molecules.

CATION EXCHANGE PROCESSES OBSERVED IN THE FEBEX FIELD EXPERIMENT (SWITZERLAND) AND IN THE PROTOTYPE REPOSITORY (PR) EXPERIMENT (SWEDEN)

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Bentonites are candidate materials for the encapsulation of radioactive waste in barrier systems in crystalline rocks. Their long-term behaviour of up to 1 million years is important to understand. Alteration of bentonites can be studied in natural analogues (illitization, alkaline plume) and in laboratory experiments at numerous conditions. Few natural analogues exist and laboratory experiments were usually performed at unrealistic conditions such as high solution/solid ratios and dynamic (batch) experiments. Important knowledge about bentonite performance is gained from large-scale experiments in different underground rock laboratories with different type of groundwater.

The "full-scale engineered buffer experiment" (FEBEX) was installed in Grimsel, Switzerland, with a low salinity groundwater: Na-Ca-HC03-F type with 0.7 mM Na^+ and 0.14 mM Ca^{2+}. Other cations are present in traces: 2.1 µM Mg^{2+}, 2.3 µM Sr^{2+}, and 3.6 µM K^+; the pH in 9.6 (Degueldre, 1994, table 3 for GTS). The FEBEX experiment was heated up to 100 °C for 18 years of operation.

The Prototype Repository (PR) experiment (Äspö, Sweden), on the other hand, reacted with a Na-Ca-Cl dominated groundwater (each ~ 2500 mg/L Na^+ and Ca^{2+}, ~ 8500 mg/L Cl^-, and ~ 500 mg/L SO_4^{2-}) with minor contents of Mg^{2+}, Br^-, and K^+ (all <100 mg/L). PR was heated to 65–85 °C (section 2) for 8 years.

Both experiments have been (partly) terminated recently. One of the fastest reactions that can be measured in order to study alteration of the buffer material is cation exchange. Cation exchange is important because it determines physical and chemical properties of bentonites [1].

The PR data were published before [2]. This data is compared with the recently obtained FEBEX results. In the FEBEX experiment, the distribution of exchangeable cations was investigated in different sections. All different sections showed comparable trends.

- Exchangeable Mg^{2+} shows a sharp increase towards the heater. Near the heater exchangeable Mg^{2+} was higher compared to the reference values. This differs from the PR experiment where exchangeable Mg^{2+} values were always lower compared to the reference materials with a small increase at the direct contact to the heater [2].

- Exchangeable Na^+ values were more or less unchanged over a large distance from the cold side to the hot side (heater). Closer to the heater exchangeable Na^+ values decreased in both the FEBEX and in the PR experiment.
- Exchangeable Ca^{2+} values were lower at the cold (host rock) side in FEBEX and increased (linear trend) to the hot side, whereas in the PR experiment (nearly) all values were higher than the reference values and the increase towards the heater was sharp.

The observed differences can possibly be explained by the different types of water, and secondly the maximum temperature which was lower for the PR experiment than for the FEBEX experiment. In FEBEX, however, soluble phases in the pore water have partly overprinted exchangeable cation values [3].

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HIGH TEMPERATURE STABILITY OF BENTONITE IN TWO FIELD EXPERIMENTS: ABM2 (6½ YEARS) AND ABM5 (4½ YEARS) AT ÄSPÖ UNDERGROUND LABORATORY, SWEDEN

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In Sweden radioactive waste is to be emplaced in copper canisters with iron-inserts, and the high temperature stability of bentonite is of absolute interest. In 2006, the ABM experiment started at Äspö Hard Rock Laboratory, Sweden, at 450 m depth. Twelve different clay rings (3 dm) were placed onto a heated iron cylinder (~130 °C), creating three packages (ABM1-ABM3). The first package (ABM1) was excavated in 2009 and was analyzed regarding chemistry, mineralogy, hydromechanical properties and microbiology. In 2012, three new experiments were installed (ABM45; new bentonite selection; ABM4 and 6 at 130 °C, and ABM5 initially at 80 °C). In 2013, the second package (ABM2) was excavated, 6½ years after installation, and in 2017, the ABM5 was excavated after 4½ years of heating. The ABM3 is expected to be excavated in about 2023 (17 years after installation).

In ABM2, in the close contact with the iron heater at Febex bentonite block 9 a sample was taken mainly containing a mixture of magnetite, a trioctahedral smectite and the original smectite. The magnetite was separated with a magnet and the clay was Ca-exchanged. A new XRD reflection at 1.55 Å corresponding to a trioctahedral phase was observed. The intensity relation of the 060 reflections indicated a 35:65 relation between tri to di octahedral smectite. FT IR data using the original smectite and a ferrous reference saponite supported a 40:60 distribution. μ-RAMAN spectra were collected on 20 random ~10 x 10 μm spots, all had a similar appearance, indicating a very homogenous sample. Some dark particles ~5 x 5 μm were observed and identified as likely magnetite remainings. Accessory minerals quantified with XRD were subtracted from the chemical content of the sample. The amount of dioctahedral smectite from the 060 intensity relation was subtracted from the original pure smectite. A trioctahedral smectite should ideally have (Mg + Fe)/(Si + Al) = 0.75. The proportion of di:tri smectite was optimized using this ratio, resulting in a 40:60 distribution. The molar content of Mg was somewhat larger than Fe, hence it seems to be saponite. The thermal stability of the phase was investigated and found to be greater compared to the original smectite, which is compatible with saponite.

Traces of trioctahedral phases have been observed previously in SKB field experiments with iron, but this is the first time the phase has been characterized enough to identify it as a specific mineral. The majority of the bentonite, however, seemed fully intact.

In the final ½ year of the somewhat shorter ABM5 experiment (initially a low temperature experiment at 80 °C), the temperature was rapidly increased from 80 to approximately 200 °C in order to study the effects from thermal shock. The bentonite was highly fractured after the experiment due to the very high temperature and low pressure (atmospheric pressure in ABM5), however visual inspection could not identify any major salt accumulation due to any boiling. The lubricant present at the block surfaces (except the surface towards the heater) went black due to the burning from the high temperature. The analytical work of the ABM5 is in its early stage and mainly pictures are currently available.

TRANSFORMATION OF CLAY MINERALS DUE TO TECHNOGENIC PROCESSES ASSOCIATED WITH THE DISPOSAL OF RADIOACTIVE WASTE

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Clay minerals may transform in various systems under the influence of geological, biological or technogenic processes. The most active to the geological environment are technogenic and biochemical processes that in a relatively short time can cause transformation of the rock composition and structure and new mineral formation of minerals, especially clay minerals.

Isolation of radioactive waste is a complex technological problem. This work considers the influence of acidic and alkaline solutions involved in the radioactive waste (RW) disposal process. In the Russian Federation, due to historical reasons radioactive waste was accumulated in various types of repositories. Alongside with the near-surface repositories that are common in other countries, in the Russian Federation several facilities were using injection of liquid radioactive waste (LRW) into a sand "reservoir" layer confined between clay layers. LRW is thermodynamically unstable and highly mineralized solution of different pH and a high temperature. Changes in sand-reservoirs that occurred under the influence of injected acidic solutions at the site of the JSC "Siberian Chemical Combine" are primarily expressed in the synthesis of the peculiar smectite (montmorillonite) phase with a high sorption capacity.

Solid radioactive wastes in cement slurries at the landfill site of the Angara Electrolysis Chemical Combine (AECC) are buried in sandstones and currently suffer from the influence of highly alkaline, and highly mineralized groundwater storage area leads to a considerable transformation of the sandstones described above. This influence results in the formation of peculiar "technogenic" illites that have smectite morphology but illite structure which was confirmed by XRD data and simulating of XRD patterns. These transformations will lead to the increase of sandstone porosity and permeability.

Thus, depending on the composition of industrial waste and the properties of the geological environment, various clay minerals can be formed. That will affect the safety of the repository and must be taken into account in stability prediction.

Acknowledgments:
This work was financed by the Russian Science Foundation (Project #16-17-10270). Samples from AECC were studied with support from the Russian Foundation for Basic Research (Project #17-05-00707). XRD and SEM study was carried out on the equipment obtained with the funding of MSU Development Program.

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SPRAY DRYING – SHAPE AND SIZE OF ILLITIC CLAY GRANULES

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Clays are a unique nature resource. Clays have high surface area that can adsorb water and other valuable substances. This property is useful in cosmetics, pelotherapy, creating industrial adsorbents, etc. Clay particles are flat and tiny that makes the powder handling dusty and inconvenient. Illite clays mostly contain various other minerals. Therefore the fractionation and purification usually is done, commonly by wet methods. The drying is a crucial step to keep clays in highly dispersed state. Clays can be easily stuck in large and hard agglomerates by bulk drying. Spray drying is a powerful tool to create a round shaped agglomerates (granules) that have high flowability due to round shape. The size, hardness and composition of agglomerates are highly controllable [1].

In this study illitic clay (< 2 μm, 15 w%, pH 5 and 9 by 1M NaCl and NaOH addition) form the Iecava and Laža queries (Latvia) was dispersed in water (detailed description in [2], [3]), slurry was spray dried in lab scale BUCHI Mini Spray Dryer B-290 with two-fluid spray nozzle. Slurry feed rate was 8 mL/min. Particle mean size was detected by laser granulometry. Morphology of spray dried granules was analyzed by high field electron microscope Tescan Mira/LMU. Image processing was done by Image PRO plus 6.0, at least 200 granules.

Results showed that particle size in slurry and after re-supension is similar if sample contains no carbonates (Iecava clay), d_{50} was 1.7 μm, d_{90} was in range of 0.3–8 μm. If sample contain carbonates (Laža clay), before drying d_{50} was 1.4 to 2.1 μm and after drying it increased to 3.3-3.4 μm. The increase is due to agglomeration of particles smaller than 1 μm.

Mean spray dried granule size was 3 ± 1 μm for all samples, shape factor of granules was 1,33 ± 0,06. The distribution was not Gaussian. Smaller particles had higher shape factor, showing the non-round shape presence. This can be explained by the fact that smaller granules are parts of the larger ones. The granules containing cementitious carbonates contained less crushed particles, it can be concluded that carbonates increase the mechanical strength of particles.

It can be concluded that granules obtained by spray drying have the same size irrespective of composition. The granules that contain cementitious additive, like carbonates, are stronger and resuspend in water slower than illitic clays without carbonates. The granules without carbonates are mechanically weak and can crush even during spray drying and transportation in small volumes. The particles are round (shape factor 1.3). Therefore, for advanced use some additives should be used to increase the mechanical strength of granules.

Acknowledgments:
The research has been supported by the National Research Program of Latvia 2014–2017 within the program No. 6 project No. 4. "Investigation of geological resources – new products and technologies (Earth)".

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STUDY ON BRÖNSTED ACIDIC IONIC LIQUID ADSORPTION IN PURIFIED ILLITE CLAYS

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Clay minerals due to their nanoscale size, high cation exchange capacity and specific surface area, easy modification with organic compounds, intercalation and exfoliation potential are used as a fillers in various polymer nanocomposite (PN) synthesis. Montmorillonite clay minerals are most commonly used, however, as recently published data [1]–[3] have shown, illite clay minerals can also be used for PN application. It should be noted that application of illite clays in the PN industry is limited due to complicated illite mineral exfoliation in the polymer matrix, large quantities of associated mineral impurities and incompatibility of the hydrophilic-hydrophobic properties of the illite minerals and polymer. One of the ways to improve clay mineral dispersion in the polymer matrix is clay mineral surface modification with organic compounds.

In this study, purified Liepa deposit illite clays were chosen to modify with Brönsted acidic ionic liquids (BAIL) whose chemical structures are shown in Fig. 1. BAIL adsorption is studied for future improvement of illite clay mineral dispersion in the polymer matrix, as well as to introduce *R-SO3H* functional group that could potentially increase the proton conductivity of polymer.

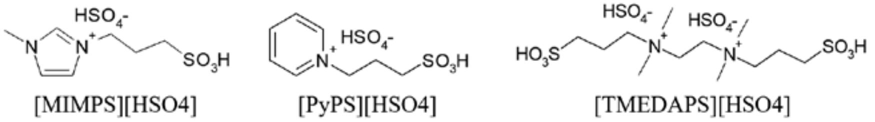

Fig. 1. Chemical structures of the Brönsted acidic ion liquids used in this study. 3-methyl-1-(3-sulfopropyl)imidazolium hydrogen sulfate [MIMPS][HSO4], 1-sulfopropyl pyridinium hydrogen sulfate [PyPS][HSO4] and N,N′-bis(3-sulfopropyl)-N,N,N′,N′-tetramethylethylene diammonium hydrogen sulfate [TMEDAPS] [HSO4].

BAIL adsorption in illite clay minerals is carried out by cation exchange reaction in aqueous solutions. Adsorption was studied by powder X-ray diffractometry, X-ray fluorescence spectrometry, differential thermal and thermogravimetric analysis, as well as by acid-base titration.

Acknowledgments:
The research was supported by the University of Latvia, grant No. 6012-A55.2/48.

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INFORMATION ABOUT SPONSORS AND EXHIBITIONS

Latvian Clay
Science Society

LATVIJAS UNIVERSITĀTE
ANNO 1919
UNIVERSITY OF LATVIA

Latvijas Universitātes
BIBLIOTEKA

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EXHIBITION AT THE UL LIBRARY "LATVIAN SCIENTISTS OF CLAY AND CERAMICS"

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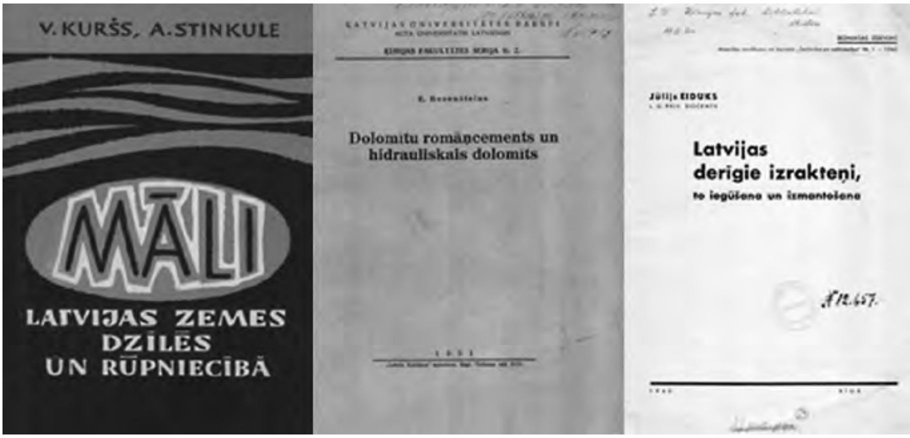
The Library of Natural Sciences of the Library of the University of Latvia (UL) (UL House of Nature, Jelgavas iela 1) invites to the exhibition "Latvian Scientists of Clay and Ceramics" open from January 29 until June 30.

The exhibition is created within the framework of the UL 76th International Conference and the 2nd International Interdisciplinary Symposium "Clays and Ceramics 2018" to mention and promote the achievements of Latvian scientists carrying out research on clay and ceramics, as well as the field of clay and ceramics and book collections of the UL Library. The information has been gathered about clay and ceramics scientists in Latvia starting from 1924. Silicate technologist Eižens Rozenšteins (1886–1933) was born in 1886, he has prepared and trained one of the leading researchers in Latvia – Jūlijs Eiduks (1904–1986). J. Eiduks collaborated with Eduards Vītiņš (1933–2011) in the analysis of clay and regarding ceramics technology in the Central Laboratory of the Department of Geology and the Protection of the Earth's Depths. Professor of UL Visvaldis Kuršs (1928–2000) in 2018 would celebrate his 90th anniversary. V. Kuršs has researched the geological structure of clay deposits, conditions of its formation and its practical use. Historical discovery has been made by scientist Jānis Sleinis, who has revealed the Liepa Devon clay fields. There is also information gathered about silicate technologist Uldis Sedmalis (1933–2017), scientists of geological exploration of clay deposits Biruta Martinsone and Eda Rinks (1909–1997), as well as the scientist of geological exploration of Jurassic clay deposits Krišs Bērziņš.

There are historically significant monographs on clay and ceramic studies in the collection of the Library of UL, which have been dedicated to important representatives of Latvian society and institutions (Fig. 1). The monograph "Latvijas derīgie izrakteņi" ("Latvian Mineral Resources") by J. Eiduks was published in 1936, the UL Library owns a copy of the monograph with dedication:


V. KURŠS, A. STINKULE

MĀLI

LATVIJAS ZEMES DZĪLĒS UN RŪPNIECĪBĀ

E. Rozenšteins

Dolomitu romāņcements un hidrauliskais dolomits

Jūlijs EIDUKS

Latvijas derīgie izrakteņi, to iegūšana un izmantošana

Fig. 1. Historically significant monographs on clay and ceramic research with authorial dedication entries.

"To the Latvian Mineral Research Society". In 1931, E. Rozenšteins published a monograph on the series of the Scientific Papers of the Faculty of Chemistry of the University of Latvia "Dolomītu romāņcements un hidrauliskais dolomīts" ("Dolomites Cement and Hydraulic Dolomite") and dedicated a copy to Latvian engineer and politician Jānis Jagars with the text "To very respectful Riga City Construction Manager, Engineer Mr. J. Jagars. With sincere greetings. Author". The scientist J. Eiduks in 1940 dedicated a monograph "Latvijas derīgie izrakteņi, to iegūšana un izmantošana" ("Mineral Resources of Latvia, their Acquisition and Use.") to "The Library of Chemistry Faculty /author/19.VI.40."

UL geologists and chemists, scientists of the field of materials science and applied chemistry of Riga Technical University and Latvia University of Agriculture nowadays research clays and ceramics.

Visitors of the exhibition "Latvian Scientists of Clay and Ceramics" can see the achievements of each scientist, photographs from internship and interesting examples of clays from the Museum of Geology at the UL Museum of Science and History of Technology.

Welcome to the library!

Exhibitions created by the Library of University of Latvia are open to viewers at the Nature House of UL:		
Atoms, energy and Curie phenomenon	The exhibition is made in honour of Polish scientist Marie Curie and her discoveries	Available until 30 April 2018
Short Moments of a Century: Rectors' Gallery	Exhibition that is dedicated to all the rectors of the University of Latvia	Available until 1 February 2018, and online www.mirkli.lu.lv.
Latvian Scientists of Clay and Ceramics	Exhibition dedicated to Latvian scientists of clay and ceramics, their research, inventions and discoveries	Available until 30 June 2018
Porcelain	Artist Jānis Ronis	Available until 30 June 2018

LATVIAN CLAY SCIENCE SOCIETY

Latvian Clay
Science Society

Latvian Clay Science Society (LCSS) is an organization that brings together scientists and other interested people in Latvia working in clay science related fields. LCSS was founded on 22 September 2015 by active scholars from various Latvian and foreign universities (University of Latvia, Riga Technical University, Poitiers University, University of Tartu). The aim of the Society is to promote scientific research in clay and clay minerals and to enhance the recognition of this research in Latvia and abroad. One of the main tasks of the LCSS is to enhance the scientific collaboration among different fields of science promoting the sharing of knowledge and the infrastructure of different scientific institutions. Other LCSS's tasks include the promotion of research in clay science among young scientists and students, as well as the collaboration with other societies in Latvia and abroad related to clay science.

The exchange of knowledge and the possibilities of collaboration are ensured by regular Board meetings at least once a month and regular meetings of all Society members at least once a semester.

To promote the research in clay science to young scientists and students, the Society organized a free two-day seminar "Clays and their characterization methods" on 1–2 February 2016. Nearly 40 participants attended the lectures of professors having received a recognition for their work in Latvian clay science research. On 28–29 January 2016, the Society participated in the organization of the 1st International Symposium "Clay and Ceramics" in the framework of the 74th Scientific Conference of the University of Latvia. The symposium was attended by researchers from the largest universities in Latvia, as well as by guests from Russia, Estonia and Denmark.

Members of the Society are actively participating in the leading conferences in the field of clay science in Europe and in the world. At the end of 2016, the LCSS received an invitation to join the European Clay Groups Association.

You are welcome to take the opportunity and become a member of Latvian Clay Science Society. Please send the application request to *info@latclay.lv*

UNIVERSITY OF LATVIA

The University of Latvia was founded in 1919 and currently, with its more than 14,000 students, 13 faculties and over 20 research institutes and independent study centres, is one of the largest comprehensive and leading research universities in the Baltics. The University offers more than 130 state accredited academic and professional study programmes. At the University of Latvia, research is conducted in over 50 research fields which represent four main areas of inquiry: the humanities, natural sciences, social sciences. The University of Latvia pays great attention to the development of international collaboration.

The objective of the University of Latvia is to develop a world-class research centre, at the same time providing research-based and innovative studies in a wide spectrum of sciences. The knowledge and technologies created at the UL are highly acknowledged internationally.

One of the UL research priorities today is to support young scientists and promote the establishment of new research groups; however, the University also focuses on matters and challenges like knowledge spillover effects and commercialization of scientific findings, science communication, internationally significant research results, development of research infrastructure, and support of research projects dedicated to the Latvian language and culture.

More information about the University of Latvia available at
https://www.lu.lv/eng/general/about-university-of-latvia/

FACULTY OF AGRICULTURE OF LATVIA UNIVERSITY OF AGRICULTURE

LF
Lauksaimniecības fakultāte

Latvia University of Agriculture (LLU) is one of the leading universities of science and technologies in the Baltic Sea region, specializing in the sustainable use of natural resources aimed at the enhancement of quality of life for society [1]. "The Faculty of Agriculture is the only place in Latvia where students can obtain a bachelor's degree, master's degree and doctoral degree in agriculture in accredited study programs. There are two institutes under the supervision of the faculty with modern training and research laboratories" [2]. Detailed information on research fields: soil science and agrochemistry, plant biology and protection, field management, crop science and production, horticulture, animal science [2], is available on *http://www.llu.lv/en/research-fields*. The soil scientists of LLU are involved in the studies of soil agroecological conditions under various management systems with the goal to exclude environmental risks and promote soil sustainability.

The students of LLU are active and show interest about knowledge in soil mineral composition – especially on clay mineralogy, therefore Latvian Clay Science Society found a possibility to give regular seminars about clays and clay minerals for clay friends in LLU from February 2018. The goal of seminars is to actualize clay science among students and other interests in any scientific discipline. We hope, that seminars will educate new generation of soil mineralogists, create friendly atmosphere and bring together clay scientists from all Latvia.

Information about seminars and research fields of the Institute of Soil and Plant Sciences of Faculty of Agriculture can be obtained from *ilze.vircava@llu.lv.*

[1] http://www.llu.lv/en/mission-and-vision
[2] http://www.llu.lv/en/faculty-of-agriculture

RIGA TECHNICAL UNIVERSITY

1862
RIGA TECHNICAL UNIVERSITY
Faculty of Materials Science and Applied Chemistry

Riga Technical University (RTU) is the only polytechnic university in Latvia and the largest university in the country – it educates and trains almost 15 thousand students. It is the largest Latvian university by number of students. Research at RTU is organized at six research platforms. The objective of research platforms is to ensure multi-faculty and interdisciplinary research in the areas of great significance for the national economy and society.

The Faculty of Materials Science and Applied Chemistry is part of "Materials, processes, and technologies" platform. The most important research directions that include investigation of clays and inorganic materials are:

- synthesis, modification, investigation and use of inorganic materials and composites for special objectives and the economy;
- innovative bioceramics (e.g. for bone tissue replacement) and composites: development material properties and production technology;
- synthesis of multifunctional nanoparticles, nanofibers and catalysts, development of nanocomposites and nanocoating production technologies from polymer and inorganic nanomaterials, products application;
- ecological solutions in chemistry, chemical engineering, materials science and allied branches.

Welcome to our international conferences:

"BaltSilica 2018" in 30 May–June 1
http://smi.rtu.lv/en

"Materials Science and Applied Chemistry – MSAC 2018" on 26 October
https://msac-conferences.rtu.lv/

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http://vkti.rtu.lv/en
http://smi.rtu.lv/en/

POWDER DIFFRACTION IN A SELF-EMPLOYED SERVICE LABORATORY
DISCUSSION OF A ROUND ROBIN OF A MINERAL SAMPLE

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First, a short introduction to the work of a self-employed service laboratory will be given.

Powder diffraction of minerals needs the attention to some specialties.

Basing on an own initiated Round Robin of a mineral sample (a mixture of 10 phases, 12 participants) the experiences will be discussed. Without any restrictions, the participants will be using different geometries, diffractometer types and programs.

- Influence of the measurement (radiation, angle range, preparation, geometry …)
- Qualitative phase analysis to find all phases
- Quantitative phase analysis (Rietveld, LOD, LOQ)
    - o Find / use of different structure data
    - o Influence / handling of absorption contrast and preferred orientations

The problems will be discussed and food for thought and solutions will be given, too.

The author is the only representative of the SiroQuant® Rietveld program in Europe.

SIROQUANT

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