Conference book / 9th Mid-European Clay Conference

09MECC

ZAGREB **CROATIA**
| 17 - 21 SEPTEMBER **2018** |

9th Mid-European Clay Conference

Conference Book

Edited by Darko TIBLJAŠ, Marija HORVAT, Nenad TOMAŠIĆ,
Marta MILEUSNIĆ & Anita GRIZELJ

9th Mid-European Clay Conference
MECC 2018

Zagreb, September 17-21, 2018

ORGANIZED BY:
Croatian Geological Society, Croatian Geological Survey, Faculty of Mining, Geology and Petroleum Engineering & Faculty of Science - University of Zagreb on behalf of the Mid-European Clay Groups

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Financed by: Croatian Science Foundation, project 2504-NanoMin "Nanominerals in sediments and soils: formation, properties and their role in biogeochemical processes"

TECHNICAL ORGANIZER:
Spektar putovanja d.o.o., Congress department, Andrije Hebranga 34, 10000 Zagreb

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PUBLISHED BY:
Croatian Geological Society, Croatian Geological Survey, Faculty of Mining, Geology and
Petroleum Engineering & Faculty of Science - University of Zagreb

ISBN:
978-953-6907-71-7 (Croatian Geological Survey)
978-953-6923-39-7 (Faculty of Mining, Geology and Petroleum Engineering - University of Zagreb)
978-953-6076-46-8 (Faculty of Science - University of Zagreb)

A CIP catalogue record for this book is available from the National and University Library in Zagreb under 001005359.

DESIGN OF COVER: Leitmotif kreativni biro j.d.o.o., IV. Maksimirsko naselje 21, 10000 Zagreb
LAYOUT AND PRINT: Laser Plus d.o.o., Brijunska 1a, 10000 Zagreb
ISSUED: 2018, 200 copies

SUPPORTED BY:
The Foundation of Croatian Academy of Sciences and Arts,
Kraneamus Krapina Neanderthal Museum,
Ministry of Science and Education of the Republic of Croatia,
Zagreb Tourist Board,
Croatian Geological Survey,
Faculty of Mining, Geology and Petroleum Engineering - University of Zagreb,
Faculty of Science - University of Zagreb

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9th Mid-European Clay Conference

CONFERENCE BOOK

(Programme, Abstracts Book and Field Trip Guide Book)

Edited by Darko TIBLJAŠ, Marija HORVAT, Nenad TOMAŠIĆ, Marta MILEUSNIĆ
& Anita GRIZELJ

Papers in this Abstracts Book were reviewed in order to correct the text and to unify their final layout.

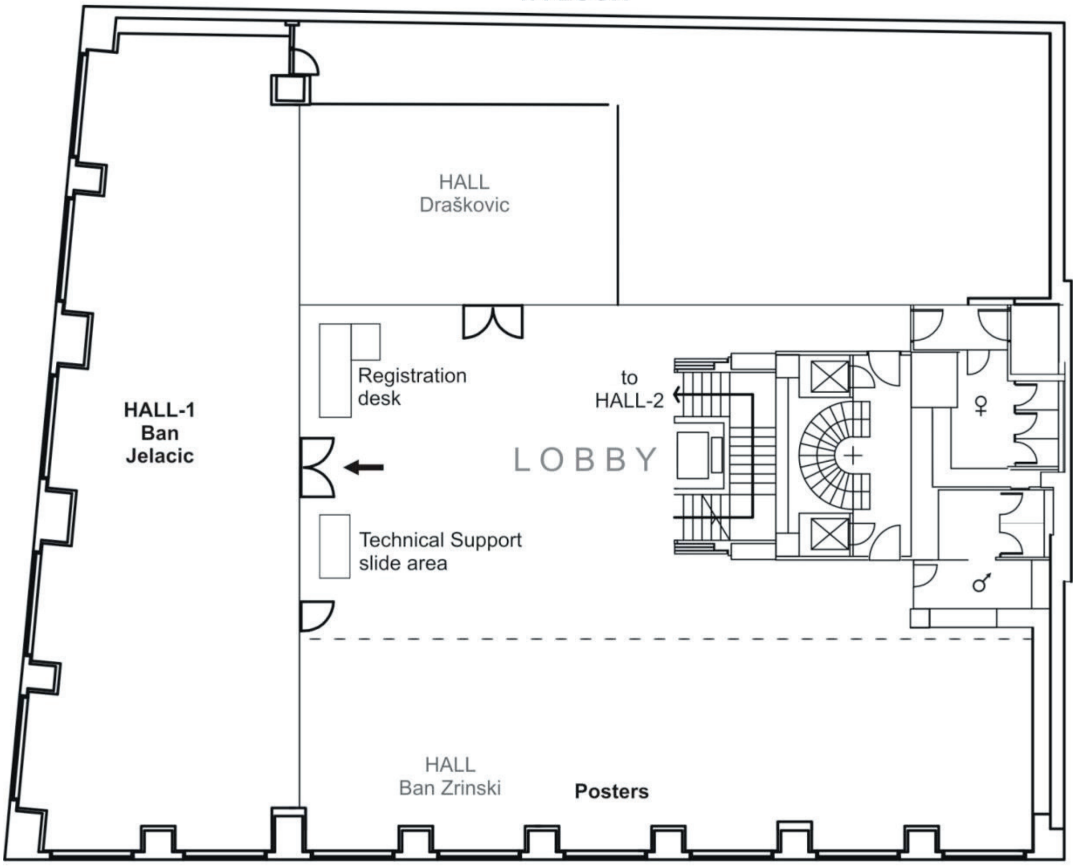
We are grateful to the reviewers:

Pilar Aranda (Spain), George Christidis (Greece), Reiner Dohrmann (Germany), Barbora Dousova (Czech Republic), Goran Durn (Croatia), Liva Dzene (France, Latvia), Rafael Ferreiro Mählmann (Germany), Saverio Fiore (Italy), Stephen Hillier (UK), Miroslav Honty (Belgium), Asuman Günal Türkmenoğlu (Turkey), Reinhard Kleeberg (Germany), Biljana Kovačević Zelić (Croatia), Sofia N. Lessovaia (Russia), Jana Madejová (Slovakia), Marta Mileusnić (Croatia), Ana Petkovšek (Slovenia), Michael Plötze (Switzerland), Miroslav Pospíšil (Czech Republic), Béla Raucsik (Hungary), Fernando Rocha (Portugal), Jan Środoń (Poland), Darko Tibljaš (Croatia), Nenad Tomašić (Croatia), Peter Uhlík (Slovakia), Bella Zviagina (Russia)

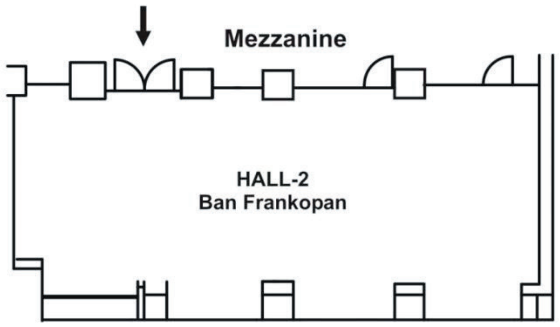
Monday, September 17th- Registration (Hotel Dubrovnik, close to the Hotel Reception)
other days - Registration (in the Lobby of Hotel Dubrovnik Congress Center)

CONGRESS CENTER

1. FLOOR



Mezzanine



EVENTS SCHEDULE

Monday, September 17th

13:30-18:30	Registration (Hotel Dubrovnik, close to the Hotel Reception)
19:00-21:00	Welcome reception (Hotel Dubrovnik, Ban Jelačić Hall)

Tuesday, September 18th

8:30-9:00	Opening Ceremony (Hotel Dubrovnik, Ban Jelačić Hall)
19:10-20:10	DTTG Board Meeting (Hotel Dubrovnik, Ban Frankopan Hall)

Wednesday, September 19th

14:00-16:00	Zagreb guided city tour
20:00-24:00	Conference dinner (Vinodol Restaurant, Nikole Tesle 10)

Thursday, September 20th

19:00-20:00	DTTG Meeting (Hotel Dubrovnik, Ban Jelačić Hall)
20:30	Mid-European Clay Societies Representatives Meeting

Friday, September 21st

12:35	Closing Ceremony (Hotel Dubrovnik, Ban Jelačić Hall)

Saturday, September 22nd

	Field trip to Hrvatsko Zagorje

Tuesday, September 18th

BAN JELAČIĆ HALL
8:30-9:00 Opening Ceremony
9:00-9:45 Plenary lecture:
Clay mineralogy and the origin of unconventional Paleozoic shale reservoirs from the North American midcontinent
Branimir Šegvić, Giovanni Zanoni, Dustin E. Sweet and Andrea Moscariello
(introduced by Jan Środoń)

BAN JELAČIĆ HALL Session E Clay (and associated) minerals in geological systems Chairs: Jan Środoń and Rafael Ferreiro Mählmann	**BAN FRANKOPAN HALL** Session C Modification and synthesis of clays Chairs: Pilar Aranda and Liva Dzene
9:50 – 10:10 Weathering crusts, clay mineralogy and tectonic quiescence: preliminary results Michael Jeffrey Wilson, Mikhail Viktorovich Shaldybin and Lyudmyla Wilson	9:50 – 10:10 Synthesis of dioctahedral clay minerals under low temperature hydrothermal conditions for different time periods Elif Vargun, Ceren Küçükuysal, Ömer Bozkaya, Sabine Petit, Merve Gulcan and Zeynep Akçay Yaylim
10:10 – 10:30 Paleoenvironmental and paleoclimatological assessment of the Kalecik basin based on multi-proxy data from the lake sediments of the Neogene Hançılı Formation, Central Turkey Serdar Aker, Asuman Günal Türkmenoğlu and Ceren Küçükuysal	10:10 – 10:30 Formation of iron-rich phyllosilicates in Si-Fe system in function of Fe/Si molar ratio Liva Dzene, Jocelyne Brendle, Lionel Limousy, Patrick Dutournie, Christelle Martin and Nicolas Michau
10:30 – 10:50 Pore-scale processes in clay-bearing chalks: an example from the Outer Carpathians (Poland) Katarzyna Górniak	10:30 – 10:50 Application of halloysite impregnated with Fe^0 particles for acid mine drainage water treatment Paulina Maziarz and Jakub Matusik

10:50 – 11:20 COFFEE BREAK

BAN JELAČIĆ HALL Session E Clay (and associated) minerals in geological systems Chairs: Jan Środoń and Rafael Ferreiro Mählmann	**BAN FRANKOPAN HALL** M General session Chairs: Marta Mileusnić and Franz Ottner
11:20 – 11:40 Geology, mineralogy, geochemistry and genesis of bentonite deposits in Miocene volcano-sedimentary units of the Balıkesir region, western Anatolia Selahattin Kadir, Tacit Külah, Hülya Erkoyun and Raffi Arslanyan	11:20 – 11:40 Investigation of the surface sites of tubular halloysite using phosphate anions Nia Gray, Stephen Hillier, Peter Holliman, Chris Greenwell and David Lumsdon
11:40 – 12:00 The nature, origin and significance of luminescent layers in the Bazhenov Shale Formation of West Siberia, Russia Michail V. Shaldybin, Michael J. Wilson, Lyudmyla Wilson, Yuriy M. Lopushnyak and Elena S. Deeva	11:40 – 12:00 Healing clays from Santa Maria (Azores, Portugal): assessment of their potentialities Ângela Cerqueira, Cristiana Costa, Fernando Rocha, Cristina Sequeira and Denise Terroso
12:00 – 12:20 Artificially induced clay mineral authigenesis in an underground gas storage field, North Alpine Foreland Basin, Austria Magdalena Bottig, Susanne Gier and Wolfdietrich Jilg	12:00 – 12:20 Study of iontophoresis process using clays as a transdermal drug delivery system Carla Marina Bastos, Fernando Rocha, Amélia P. Marinho, Ângela Cerqueira and Nuno Gomes

	12:20 – 12:40 Ethnopharmacological use of geophagic clays Fernando Rocha, Ângela Cerqueira, Carla Marina Bastos and Cristiana Costa

12:40 – 13:50 LUNCH BREAK

BAN JELAČIĆ HALL Session G Clays in soils and young sediments Chairs: Goran Durn and Sofia Lessovaia	**BAN FRANKOPAN HALL** Session H Clays and environment protection Chairs: Barbora Doušová and Miroslav Honty
13:50 – 14:10 Effect of particle shape and surface charge properties on the formation and stability of microaggregates Stefan Dultz, Georg Guggenberger, Robert Mikutta, Martin Schrapel and Susanne K. Woche	13:50 – 14:10 Use of Fe/Mn – modified aluminosilicates as selective anionic sorbents Barbora Dousova, David Kolousek, Miloslav Lhotka and Vladimir Machovic
14:10 – 14:30 Synthesis and multi-analytical characterization of hydroxy-interlayered smectite (HIS) Jan Dietel, Jens Gröger-Trampe, Marko Bertmer, Stephan Kaufhold, Kristian Ufer and Reiner Dohrmann	14:10 – 14:30 Influence of the synthesis precursors of layered double hydroxides on the removal of chromium species from aqueous solutions Magdalena Costanzo, Cecilia Ávila, Nora A. Comelli and Nora A. Merino
14:30 – 14:50 Application of high gradient magnetic separation for characterization of glauconite weathering products formed in soils under different pH conditions Magdalena Skoneczna, Michał Skiba, Katarzyna Maj-Szeliga and Wojciech Szymański	14:30 – 14:50 International Bentonite Longevity (IBL) project: an overview William Russell Alexander, Masakazu Ito and Heini Maria Reijonen
14:50 – 15:10 Mineralogical and geochemical study of the marine sediments of south Aegean Sea: implications for provenance Georgia Leontopoulou, George E. Christidis, George Papatheodorou, Maria Geraga and Gregory Roussakis	14:50 – 15:10 Application of silver- bentonite in nuclear waste treatment Dóra Buzetzky, Zoltán Nemes, Nagy M. Noémi and József Kónya
15:10 – 15:30 Clay mineralogy of sediments from the Vistula River and the Gdańsk Bay (Poland) Marta Kisiel, Michał Skiba, Artur Kuligiewicz, Mateusz Damrat, Katarzyna Maj-Szeliga and Marek Zajączkowski	15:10 – 15:30 Competitive adsorption of Cs and Sr onto raw and amphoteric surfactant-modified Laponites® Thomas Thiebault, Jocelyne Brendlé, Grégoire Augé and Lionel Limousy

15:30 – 16:00 COFFEE BREAK

BAN JELAČIĆ HALL Session G Clays in soils and young sediments Chairs: Goran Durn and Sofia Lessovaia	**BAN FRANKOPAN HALL** Session A Crystal chemistry and structure of clay minerals Chairs: Stephen Hillier and Kristian Ufer
16:00 – 16:20 Red soils in Mugla polje, SW Turkey: Mineralogical and Geochemical Approach Ceren Küçükuysal, Murat Gul, Tural Aghayev and Merve Gulcan	16:00 – 16:20 About the relation of tetrahedral Fe, tetrahedral charge, and Fe-content of dioctahedral smectites Stephan Kaufhold

16:20 – 16:40 Clay mineralogy of soils developed on Miocene marl sections of Mt Medvednica, NW Croatia: Origin and transformation in temperate humid climate Zvonka Gverić, Štefica Kampić, Anja Paradžik, Pavo Vrbanec and Nenad Tomašić	16:20 – 16:40 Structural iron release from bentonite by Y^{3+} and La^{3+} ions Eszter Mária Kovács, József Kónya and Noémi Nagy
16:40 – 17:00 Clay mineralogy of the soils from high belt of the Altai Mountains Sofia N. Lessovaia, Michail Amosov and Kirill Chistyakov	16:40 – 17:00 Order-disorder in Mg-Fe chlorites with semi-random stacking based on powder X-ray diffraction data Katarzyna Luberda-Durnaś, Marek Szczerba, Małgorzata Lempart and Arkadiusz Derkowski
	17:00 – 17:20 Structural transformation of lepidocrocite-type layered titanate, $Cs_{0.8}Ti_{1.6}Ni_{0.4}O_4$, via acid treatment and subsequent calcination at different temperatures Kanji Saito, Yusuke Komiya, Minoru Sohmiya, Masataka Ogasawara and Sumio Kato

BAN ZRINSKI HALL
POSTERS – 17:20-19:00

Session A Crystal chemistry and structure of clay minerals

A-1 Structural analysis of beidellite and montmorillonite intercalated with acetylcholine and choline – computational investigation
Peter Škorňa, Eva Scholtzová, Ľuboš Jankovič and Daniel Tunega

A-2 The combination of different disorder models for the Rietveld refinement of rectorite, a regular interstratified clay mineral
Kristian Ufer, Jan Dietel, Stephan Kaufhold and Reiner Dohrmann

Session B Physico-chemical properties of clays

B-1 Removal of spiramycin from aqueous solutions using natural and purified Algerian palygorskite
Lala Setti Belaroui, Abderrahman Habibi, Alberto Lopez Galindo and Aránzazu Peña

B-2 Textural characteristics of rehydroxylated kaolinites
Miloslav Lhotka and Barbora Dousova

Session D Organoclays and nanocomposites

D-1 Influence of quaternary alkylphosphonium and alkylammonium cations on the interaction of synthetic saponite with laser dye
Martin Barlog, Helena Pálková and Juraj Bujdák

D-2 Near-infrared spectroscopy: the useful tool for monitoring the conformations of organic cations during hydration and dehydration
Valéria Bizovská, Ľuboš Jankovič and Jana Madejová

D-3 Highly ordered α-zirconium phosphate intercalate with p-aminoazobenzene: structure refinement and interaction with UV radiation revealed by molecular modelling
Anna Koteja, Katarzyna Luberda-Durnaś, Marek Szczerba and Jakub Matusik

D-4 DFT study of atrazine-beidellite intercalate
Daniel Moreno Rodríguez, Eva Scholtzová and Ľuboš Jankovič

D-5 The application of NIR spectroscopy for monitoring the conformation of a series of primary amines in montmorillonite interlayers
Michal Slaný, Ľuboš Jankovič and Jana Madejová

Session E Clay (and associated) minerals in geological systems

E-1 Clay minerals in the Upper Permian evaporite deposits from the Mali Kukor, Vranjkovići, and Slane Stine (Dalmatia, Croatia)
Željko Dedić, Nikolina Ilijanić and Slobodan Miko

E-2 Mineralogical and geochemical characterization of Quaternary lacustrine sediments in Rečica clay deposit (Croatia)
Erli Kovačević Galović, Nikolina Ilijanić, Slobodan Miko and Željko Kastmüller

E-3 Geochemical and mineralogical signatures of Istrian Lower Palaeogene bauxites – a geodynamical thread
Zoran Peh, Nikolina Ilijanić, Slobodan Miko and Erli Kovačević Galović

E-4 Stratigraphic distribution and lithofacial variations of Carboniferous shales
Eva Wegerer, Nicolai Aust and Alessandra Rachetti

E-5 Smectite stability in alternating mudstone-sandstone facies from the Pennsylvanian Hoxbar Group (Anadarko Basin, Oklahoma)
Giovanni Zanoni, Branimir Šegvić, Jordan Coe and Dustin E. Sweet

Session F Investigation methods of clays and clay minerals

F-1 Effect of disaggregation energy on amounts of clay fractions and the clay mineralogy inventory
Reiner Dohrmann

F-2 Near-IR spectroscopy in organoclays study
Jana Madejová

F-3 Mathematical model of methylene blue dimerization on clay surfaces
Maja Milošević and Mihovil Logar

Session G Clays in soils and young sediments

G-1 Clay minerals in Icelandic soils - a study on the weathering of tephra and how they impact soil development in South East Iceland
Theresa Bonatotzky, Franz Ottner, Egill Erlendsson and Guðrún Gísladóttir

G-2 Geochemistry of volcanic clayey soils from Santa Maria (Azores, Portugal)
Ângela Cerqueira, Cristiana Costa, Fernando Rocha, Cristina Sequeira and Denise Terroso

G-3 The influence of Fe-oxides and organic matter on surface properties of nanostructured microaggregates of the Terra rossa and Calcocambisol
Stanko Ružičić, Goran Durn, Ivan Sondi, Nuša Cukrov, Srečo D. Škapin and Neda Vdović

G-4 Mineralogical characterisation of Batizovské pleso sediments (High Tatras, Slovakia)
Peter Uhlík, Adrian Biroň, Radovan Pipík, Juraj Šurka, Dušan Starek and Rastislav Milovský

Session H Clays and environment protection

H-1 Stability of Fe-containing minerals in the oxidized zone of the Boom Clay
Miroslav Honty, Lian Wang, Christophe Bruggeman, Thomas Bakas, Jana Madejová and Xavier Sillen

H-2 Sorption of Ni^{2+} and Zn^{2+} on selected natural and synthetic materials
Tomáš Binčík, Marek Osacký and Martina Vítková

H-3 The influence of zeolites from Donje Jesenje area on the removal of lead and cobalt from water
Tea Novaković and Filip Sokol

Session I Clays in geotechnical applications

I-1 The stability of bentonites in aqueous solutions (25 to 120°C) relevant to the underground sealing of radioactive waste deposits
Georg H. Grathoff, Carolin Podlech, Laurence N. Warr and Arthur Meleshyn

I-2 Impact of polymer-characteristics on the hydro-mechanical properties of polycationic modified bentonite
Wolfgang Lieske and Gemmina Di Emidio

Session J Industrial application of clays

J-1 Evaluation of bentonite deposits from Greece for industrial applications
Eleni Koutsopoulou, George E. Christidis and Ioannis Marantos

J-2 Removal of iron during bleaching of Bulgarian kaolins
Kremena Mincheva, Aylin Dzhelyaydinova, Veselina Stefanova and Jivka Ivanova

J-3 Removal of heavy metals from polluted soil using zeolites synthesized from perlite by-product material
Marek Osacký, Martina Vítková, Helena Pálková, Ľuboš Jankovič, Adriana Czímerová, Pavol Hudec and Jaroslav Sedláček

M General session

M-1 Sediments lagoons characterization to be used as a therapeutic muds in thalassotherapy
Cristiana Costa, Ângela Cerqueira and Fernando Rocha

M-2 Roman pottery workshops in the province Dalmatia: identifying clay sources and production technology through mineralogical analysis
Anita Grizelj and Ana Konestra

M-3 Palaeoenvironmental reconstruction of a Permian playa lake: the Boda Claystone Formation
Amadé Halász

M-4 Structural description and properties of Mg_2Al-layered double hydroxides intercalated with the fluvastatin anions solved by molecular simulation methods
Milan Pšenička and Miroslav Pospíšil

M-5 LDH as a drug nanocarrier described by DFT and MD calculation methods
Milan Pšenička, Jakub Škoda and Miroslav Pospíšil

M-6 Biogeochemical characterization of sediments under the anthropogenic influence at mouth of Rio de Minas, Punta Arenas, Chile
Vladimir Bermanec, Jasna Hrenović, Snježana Kazazić, Erna van Wilpe, Chantelle Venter and André Botha

M-7 Characterization of bacteria in nickel-rich kaolinite, montmorillonite, and saponite mixture from Gornje Orešje, Croatia
Vladimir Bermanec, Jasna Hrenović, Snježana Kazazić, Erna van Wilpe, Chantelle Venter and André Botha

Wednesday, September 19th

BAN JELAČIĆ HALL
8:30-9:15 Plenary lecture:
Thermal reactions of clay minerals and implication for applications
Katja Emmerich
(introduced by Reinhard Kleeberg)

BAN JELAČIĆ HALL Session F Investigation methods of clays and clay minerals Chairs: Reinhard Kleeberg and Jana Madejová	**BAN FRANKOPAN HALL** Session E Clay (and associated) minerals in geological systems Chairs: Asuman Günal Türkmenoğlu and Béla Raucsik
9:20 – 9:40 Applying a thermogravimetric quantitative method for the determination of dehydroxylation and dehydrogenation in Fe-chlorites Małgorzata Lempart and Arkadiusz Derkowski	9:20 – 9:40 Clay mineralogy of the Kışladağ porphyry Au deposit (Uşak, western Turkey): Evidence for an epithermal overprint Ömer Bozkaya, Nurullah Hanilçi, Gülcan Bozkaya, David Banks and I. Tonguç Uysal
9:40 – 10:00 Cation exchange capacity of bentonite in highly saline environment Peter Boháč, Laure Delavernhe, Erik Zervas, Franz Königer, Rainer Schuhmann and Katja Emmerich	9:40 – 10:00 Genesis of the Yarıkçı hydrothermal kaolinite deposit within Paleozoic metamorphic units, Mihalıççık, Eskişehir, Turkey Selahattin Kadir, Hülya Erkoyun and Tacit Külah
10:00 – 10:20 Significant bias in clay minerals extracted from ancient carbonates? Rute Coimbra, Fernando Rocha, Adrian Immenhauser, Federico Olóriz, Denise Terroso and Mauritz Horikx	10:00 – 10:20 Illites and chlorites in hydrothermal alteration of a shallow-dipping epithermal Au-Ag-Pb-Zn-Cu deposit Banská Hodruša, Slovakia Peter Koděra, Peter Uhlík, Adrian Biroň, Alexander Kubač, Boris Bača and Marek Osacký

10:20 – 10:50 COFFEE BREAK

BAN JELAČIĆ HALL Session F Investigation methods of clays and clay minerals Chairs: Reinhard Kleeberg and Jana Madejová	**BAN FRANKOPAN HALL** Session E Clay (and associated) minerals in geological systems Chairs: Asuman Günal Türkmenoğlu and Béla Raucsik
10:50 – 11:10 Benefits of 3D X-ray tomography (XCT) analysis on textural bentonite characterisation Heini M. Reijonen, Jukka Kuva and Heidi Laxtröm	10:50 – 11:20 Keynote lecture Preliminary attempt to define grade of diagenesis and incipient metamorphism considering geothermal gradients calibrated with clay mineral, mineral and maceral index data Rafael Ferreiro Mählmann
11:10 – 11:30 Combined ab initio and XAFS spectroscopy study on the characteristics of metal uptake by clay minerals Annamária Kéri, Rainer Dähn, Matthias Krack and Sergey V. Churakov	11:20 – 11:40 Illitization age data on pre-Alpine geological events: an example from the autochthonous Paleozoic sequence, Tauride Belt, Southern Turkey Ömer Bozkaya, Hüseyin Yalçın, I. Tonguç Uysal, Mehmet Cemal Göncüoglu, Rafael Ferreiro Mählmann and Cengiz Okuyucu
11:30 – 11:50 Use of SWIR spectroscopy for the exploration of permeable fracture zones in geothermal wells exploiting a deep-seated granite reservoir Carole Glaas, Jeanne Vidal, Benoit Hébert, Patricia Patrier, Daniel Beaufort and Albert Genter	11:40 – 12:00 Elemental mobilization during burial diagenesis of illite-smectite mixed-layer clays in the Beaufort-Mackenzie Basin, Arctic Canada Jaehong Ko and Reinhard Hesse

11:50 – 12:10 Detection and quantification of TiO_2 polymorphs in kaolins by X-ray diffraction Helen Pendlowski, Stephen Hillier and Ian Phillips	12:00 – 12:20 Thermal history of the central part of the Karst Dinarides, Croatia: combined application of clay mineralogy and low-T thermochronology Jan Środoń, Aneta A. Anczkiewicz, István Dunkl, Igor Vlahović, Ivo Velić, Bruno Tomljenović, Tadeusz Kawiak, Michał Banaś and Hilmar von Eynatten
12:10 – 12:40 Keynote lecture Strategies of background treatment in X-ray powder diffraction analysis of clays Reinhard Kleeberg	

12:40 – 13:45 LUNCH BREAK

14:00 – 16:00 ZAGREB GUIDED CITY TOUR

20:00 – 24:00 CONFERENCE DINNER

Thursday, September 20th

8:30-9:15 Plenary lecture:
Functional nanostructured materials by assembling fibrous clays and other nanoparticles
Pilar Aranda
(introduced by Miroslav Pospíšil)

BAN JELAČIĆ HALL Session J Industrial application of clays Chairs: George Christidis and Peter Uhlík	**BAN FRANKOPAN HALL** NanoMin workshop Chairs: Ivan Sondi and Goran Durn
9:20 – 9:40 Laponite® technology: present status, challenges and future trends Kirill Shafran and Jane Doyle	9:25 – 10:10 Understanding the (paleo)soils: From palaeoenvironmental reconstruction to the role of iron oxides and soil organic matter on the formation of the surface physicochemical properties and the aggregation processes Goran Durn, Ivan Sondi, Srečo D. Škapin, Marta Mileusnić, Thilo Rennert, Nuša Cukrov, Vedran Rubinić and Stanko Ružičić
9:40 – 10:00 Russian bentonite clay deposits: geological occurrences, structure and properties Peter Belousov, Sergey Zakusin, Olga Dorzhieva, Ekaterina Typina and Victoria Krupskaya	
10:00 – 10:20 Rheological properties of bentonite and palygorskite suspensions after dynamic aging at high temperatures George E. Christidis, Sophia Lytra, George Vlachos and Demetrios Marinakis	10:10 – 10:40 Nanosized and nanostructured mineral phases from recent sediments and soils of the Adriatic region Ivan Sondi, Srečo D. Škapin and Goran Durn
10:20 – 10:40 Effect of calcined bentonite as a supplementary cementitious material on the long-term performance of concrete André Trümer, Horst-Michael Ludwig, Matthias Schellhorn and Ralf Diedel	

10:40 – 11:10 COFFEE BREAK

BAN JELAČIĆ HALL Session J Industrial application of clays Chairs: George Christidis and Peter Uhlík	**BAN FRANKOPAN HALL** NanoMin workshop Chairs: Ivan Sondi and Goran Durn
11:10 – 11:30 Development of special clay blends for fibre reinforced plasterboards to improve fire resistance Matthias Schellhorn, Dirk Stiehl and Ralf Diedel	11:10 – 11:40 Formation of the authigenic cements in aquatic sediments through precipitation processes at the nanoscale - isotopic and FESEM study Sonja Lojen, Srečo D. Škapin, Maja Ivanić, Tamara Troskot-Čorbić and Ivan Sondi
11:30 – 11:50 Adobe formulations for rehabilitation of old buildings (in Portugal) Cristiana Costa, Ana Velosa, Sara Moutinho, Ângela Cerqueira and Fernando Rocha	
11:50 – 12:10 Effect of talc, huntite, and magnesitic clay and sepiolitic–dolomite additions as different MgO sources on physical properties of Ca-rich ceramic bodies Aydın Aras	11:40 – 12:10 Size-related mineralogical and surface physico-chemical properties of inorganic colloidal particles in recent marine sediments of the Adriatic Maja Ivanić, Ivan Sondi, Goran Durn and Srečo D. Škapin
12:10 – 12:30 Influence of clay mineralogy for heavy clay products Alexander Eppner	

12:30 – 13:40 LUNCH BREAK

BAN JELAČIĆ HALL

13:40-14:25 **George Brown lecture:**
Quantitative analysis of clay minerals and poorly ordered phases by prior determined X-ray diffraction full pattern fitting: procedures and prospects
Stephen Hillier

14:25-15:10 **Gerhard Lagaly Award lecture:**
About relations of properties and performances of bentonites
Stephan Kaufhold

15:10 – 15:35 COFFEE BREAK

BAN JELAČIĆ HALL Session J Industrial application of clays Chairs: George Christidis and Peter Uhlík
15:35 – 15:55 Recycling of rare earth elements from electronic wastes by selective adsorption on industrial clay minerals Stefan Ginzel, Christoph Piribauer, Sarah Klecha, Ralf Diedel and Joachim Scholz
15:55 – 16:15 Removal of chromates and arsenates by halloysite-LDH composites Jakub Matusik and Jakub Hyla
16:15 – 16:35 Computational modelling of the interactions of kaolinite with heavy oil components in solution Stanislav R. Stoyanov, Feng Lin and Yuming Xu

16:35 – 17:00 COFFEE BREAK

BAN JELAČIĆ HALL Session B Physico-chemical properties of clays Chairs: Reiner Dohrmann and Miroslav Pospíšil
17:00 – 17:20 Mg–Fe LDH derived from magnesite and hematite and its affinity towards sulphates Karolina Rybka and Jakub Matusik
17:20 – 17:40 Characterization of Tagaran natural clays and its use as adsorbent for removal of a model cationic dye Dler M. Salh, Bakhtyar K. Aziz and Stephan Kaufhold
17:40 – 18:00 Molecular mechanism of dissolution, growth and ion incorporation of clay minerals at the mineral/water interface René Schliemann, Inna Kurganskaya and Sergey V. Churakov
18:00 – 18:20 High-pressure methane adsorption on Cs-montmorillonite: experiments and Monte Carlo modelling Paweł P. Ziemiański, Marek Szczerba and Arkadiusz Derkowski
18:20 – 18:40 Kinetics of rehydroxylation in dioctahedral 2:1 clay minerals: reaction mechanisms and implications for archeometric dating Artur Kuligiewicz and Arkadiusz Derkowski

Friday, September 21st

8:30-9:15 Plenary lecture:
Clays in earthworks - importance of soil water retention curve
Ana Petkovšek
(introduced by Michael Plötze)

BAN JELAČIĆ HALL
Session I Clays in geotechnical applications
Chairs: Biljana Kovačević Zelić and Michael Plötze

9:20 – 9:40
Comparison of swelling behaviour and hydraulic conductivity of clay pellets for sealing purposes in the framework of geotechnical applications

Florian Christ, Matthias Schellhorn and Wiebke Baille

9:40 – 10:00
Hydro-mechanical behaviour of the MX-80 bentonite and bentonite-sand mixture hydrated with brine

Richard Brachman, Grant Su, Kerry Rowe, Anil Aickel, Son Nguyen, Karina Lange and Julie Brown

10:00 – 10:20
Shear strength anisotropy of clays from Bedekovčina region in Croatia

Aleksej Aniskin, Matija Orešković and Božo Soldo

10:20 – 10:40
The role of clay minerals in formation of sliding surface – a case study of Črešnjevec landslide (Zagreb, Croatia)

Jasmina Martinčević Lazar, Željko Miklin, Laszlo Podolszki, Goran Durn and Anita Grizelj

10:40 – 11:00
Influence of organic matter on soil mechanical properties

Michael Plötze

11:00 – 11:30 COFFEE BREAK

BAN JELAČIĆ HALL
M General session
Chairs: Fernando Rocha and Nenad Tomašić

11:30 – 11:50
Impact of mineralogy and pore water chemistry on the CEC of the Boom Clay (Belgium)

Lander Frederickx, Miroslav Honty, Mieke De Craen, Reiner Dohrmann and Jan Elsen

11:50 – 12:10
Hectorites from the Lyles deposit, Arizona, USA, and Agua Fria, Sonora, Mexico

Mathias Köster and H. Albert Gilg

12:10 – 12:30
Detailed study on origin, geology and mineralogy of Ahırözü Kaolin Deposits, Mihalıççık, Eskişehir-Turkey

Işıl Ömeroğlu Sayıt, Asuman Günal Türkmenoğlu and Ş. Ali Sayın

12:35 Closing Ceremony

LUNCH

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NanoMin Workshop

Functional nanostructured materials by assembling fibrous clays and other nanoparticles

Pilar Aranda

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Layered clay minerals, such as montmorillonite and other smectites, have been largely used for developing diverse nanostructured porous materials by generation of metal oxide nanoparticles in their interlayer region (e.g., pillared clays). In recent years, sepiolite and palygorskite fibrous clay minerals are attracting increasing interest as promising nanoplatforms for the immobilization of many diverse nanoparticles (NP), producing nanostructured materials for diverse advanced applications such as adsorbents and catalysts for environmental remediation, photoactive materials, electrochemical devices and controlled drug delivery. Sepiolite and palygorskite present a relatively large external surface area and external silanol groups regularly located along the fiber, allowing their assembly to many different types of NP. The resulting heterostructured materials are usually very stable and the presence of the clay offers the possibility of incorporation additional functionalities, giving rise to multifunctional nanoplatforms. This communication will introduce examples from our Group´s experience to show how sepiolite can act as a convenient nanoplatform for immobilization of diverse type of nanoparticles, such as TiO_2, ZnO, Fe_3O_4, Prussian blue, zeolites, layered double hydroxides (LDH), carbon nanotubes and graphenes, etc. for producing functional materials for applications in diverse fields (e.g., catalysis, environmental remediation, energy production,..). Amongst the most typical methodologies that can be used to prepare some of these nanostructured materials are those based on the in situ growing of the NP, which can be applied to produce metal oxide NP and other crystalline solids such as nano-zeolites, LDH, magnetite or Prussian blue, which become anchored to the clay fibers by interaction with their silanol groups. The use of organic–inorganic interfaces involving for instance organoclays or/and NP modified with organic functionalities at their external surface (e.g., a ferrofluid of Fe_3O_4-oleic acid NP) may simplify and in certain cases also helps to control the formation of the nanostructured material. Moreover, in certain conditions it is possible to produce the direct assembly of sepiolite and other NP, such as carbon nanotubes, graphene nanoplatelets, or even other clays particles, using ultrasound irradiation. Finally, with the reported examples it will also show how one of the additional advantages of using sepiolite as nanoplatform is the possibility to incorporate other species associated with the clay (e.g., organic molecules, etc.) and so to produce multifunctional materials.

Acknowledgments
This study was financed by the MINECO, Spain (project MAT2015-71117-R).

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Thermal reactions of clay minerals and implication for applications

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Clays and soils are ubiquitous and consist of a complex mixture of clay minerals and various amounts of other minerals, X-ray amorphous phases and organic matter. Because of a composition regarded too complex for chemical analysis to furnish any precise data on the structures of their components clays were among the first materials studied in the course of the development of thermal analysis (TA) at the end of the 19th century (LE CHATELIER, 1887). Later the thermal behaviour of clay minerals could be related to their structure (e.g. CAILLERE & HENIN, 1948; COLE, 1955; MACKENZIE, 1957; MACKENZIE & BISHUI, 1958). Finally, the work of DRITS et al. (1995) enabled comprehensive and unambiguous classification of turbostratic disordered smectites (EMMERICH et al., 2009; WOLTERS et al., 2009). The present use of TA for characterization of clays and clay minerals was stimulated by the development of advanced coupling of TA techniques for simultaneous thermal analysis (STA), the increased interest in hydration behaviour of clay minerals and the "rediscovery" of puzzolanic properties and reactivity of calcined clays for supplementary cementitious materials (SCMs) and geopolymers.

Clay minerals undergo four thermal reactions during STA with increasing temperature: dehydration (endothermic), dehydroxylation (endothermic), decomposition (endothermic) and recrystallization of high temperature phases (exothermic). The thermal modification of clay minerals and the occurrence of diagnostic thermal reactions depends not only on the structure of clay minerals but also on size of the already minute particles, admixtures and naturally on the experimental conditions. Therefore, standardized conditions for STA are essential but in any case, STA is an invaluable complementary tool to other mineralogical methods (e.g. vibrational spectroscopy, X-ray diffraction or nuclear magnetic resonance spectroscopy) and theoretical calculations to provide information on structure and thermal behaviour of clay minerals.

During the talk, few examples will be presented to illustrate how STA improved our knowledge about the relation of structure, reactivity and thermal modification of clay minerals in different applications and to describe new perspectives opened by this improvement (e.g. DIETEL et al., 2015; STEUDEL et al., 2016).

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Clays in earthworks-importance of soil water retention curve

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Saturated soil mechanics (started by Terzaghi around 1930s) defines the engineering properties of soils as a two phase system comprised of solids and incompressible pore water as a fluid. The saturated soil behaviour, such as volume changes, shear strength related slope stability and seepage are directly related to changes in the effective stress state in the soil. In saturated soil mechanics the validity of geotechnical prognoses depends on the validity and reliability of the saturated soil properties measured in situ or in the laboratory.

TERZAGHI (1936), as first, observed that fissured clays can experience some shear strength decay as a consequence of swelling induced by unloading. Many authors have report premature failures of cut slopes and embankments, constructed in stiff clays and clayey shales (ŠUKLJE, 1980; Mc GUFFEY, 1982; OAKLAND & LOVELL; 1982, MAJES, 2006). Two primary mechanisms have been recognized recently to play important roles in the softening processes: the equilibration of suction and the deterioration of fissures.

In conventional earth-works the applications of unsaturated soil mechanics still lag behind the state of the art knowledge, because the implementation of unsaturated soil mechanics is time consuming and requires expensive laboratory tests. There is also a lot of uncertainties in numerical prediction of suction changes. For these reasons a simplification was made to study the suction changes. For the purpose of design of conventional earth structures the volumetric deformations of compacted soils are mainly studied following one of the standard procedures, either by using the oedometer cell or the CBR mould in which, the unsaturated compacted specimens are flooded and the heave or the "swelling" stresses are observed without having an insight to the water content and suction changes.

There is no standardised laboratory test method available to describe these softening processes for the needs of geotechnical engineers by now. However, by the application of soil water retention curve and the in situ and laboratory suction measurements, a lot of practical engineering challenges, such as prediction of ground heave in deep cuts, prediction of strength reduction due to reduction of suction, the influence of seasonal and permanent water changes to the stiffness of embankments, can be successfully answered.

The soil water retention curve (SWRC) is the key to the implementation of unsaturated soil principles in earthworks. Historically, the first research took place in soil physics in early 1900s, mainly focused on moisture movement and the water storage in the vadose zone close to the ground surface, while the shear strength and volume changes were not of great interest. BIOT (1941), BISHOP (1959), COLEMAN (1962), MATYAS & RADHAKRISHNA (1968), FREDLUND & MORGENSTERN (1976) considered the importance of saturation (suction) to the stress paths and volume changes for different studied soils. MAČEK et al (2013) revealed that the SWRC can provide a reliable estimation of the specific surface area of inorganic soil with the total SSA greater than 5 m^2/g.

The lecture will provide the correlation between matric suction and engineering properties of highly over-consolidated clays in cuts and the correlation between matric suction and engineering properties of compacted clays and clayey shales in embankments. The importance of the pore water osmotic suction will be emphasised as well.

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Clay mineralogy and the origin of unconventional Paleozoic shale reservoirs from the North American midcontinent

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Technological advances in horizontal drilling and fracturing have greatly promoted the exploitation of hydrocarbons from fine-grained sedimentary rocks. Nowadays, the largest unconventional resources in the world are found in the Unites States spanning practically across the whole Phanerozoic, from the onset of the Paleozoic time to the Pleistocene epoch (WILSON et al., 2016). Shales are especially widespread in the Paleozoic sedimentary basins of Texas and neighboring states which unconventional shale-gas and shale-oil reservoirs commenced to play a central role in the global hydrocarbon production (e.g. CURTIS et al., 2002). As the fastest growing global energy sector, shales, and shale reservoir rocks in particular, have attracted much attention in the geological research community in the course of the past 20 years.

Clay minerals, principally dioctahedral illite and illite-smectite, make between 50 and 60 wt% of the most known shale lithologies (e.g. SHAW & WEAVER, 1965). In addition to being good indicators of sedimentary and diagenetic processes parental to these rocks, they also play a major role in defining a range of petrophysical properties of shales (e.g. porosity, permeability and fluid saturation; POTTER et al., 1980). The temperature dependent mechanism of the progressive transformation of smectite to illite through mixed-layer intermediates has been recognized as the most important diagenetic clay mineral reaction in argillaceous sediments and many authors favor this process to explain the composition of shales, suggesting an initial compositional shift from the smectitic precursor toward the random illite-smectite (e.g. ŚRODOŃ et al., 2000). There are, however, other opinions explaining a burial authigenesis in shales through direct precipitation of the compositional end-member (i.e. illite) at the expense of the previously dissolved silicate substrate (e.g. FREED & PEACOR, 1992). While the Gulf of Mexico Coast shales have been extensively studied during the last couple of decades starting with pioneer work of John Hower and his group (e.g. HOWER et al., 1976), clay mineralogy and diagenesis of Paleozoic shaly rocks of the American Midcontinent region are relatively poorly known despite the presence of the large prolific sedimentary basins that dominate the region (e.g. Permian Basin of Texas, Anadarko Basin of Oklahoma, Bend Arch–Fort Worth Basin of Texas and so on).

This study aims to determine the nature and history of the diagenesis of illitic clays from the Pennsylvanian shaly strata of the Permian and Anadarko Basins as well as the type of their precursor material(s). By testing the two competing models of illite formation (i.e. fundamental particle vs. progressive illitization of smectite), it will be possible to elucidate more on the depositional processes (type of transported material), the provenance (source lithologies), as well as several important aspects of the basinal evolution (rock cementation, hydrocarbon maturation and migration, evolution of pore water chemistry etc). A multi-methodological analytical approach is being used to find out the structural and crystalochemical characteristic of different I-S populations, as well as their age, which is pivotal for an in-depth understanding of the reaction mechanisms leading to the formation of illite-rich clay assemblages. The Pennsylvanian strata of two investigated basins represent a perfect natural laboratory to study the shale diagenesis, as they have been structurally dormant since the Early Permian time, resulting with long and undisturbed lateral continuity of shaly strata. In addition, no significant hydrothermal activity is documented that might have influenced the rates of illitization (PERRY, 1989).

Our preliminary data has shown that the studied Pennsylvanian strata (~3 km depth) consist of multiple shaly horizons interbedded with sands (Fig. 1). Two lithologies are clearly different in terms of their clay mineral content (ZANONI et al., 2018), which suggests a range of possible diagenetic pathways presumably controlled by a variable stability of smectite. Shale horizons have on average 35 % of clay minerals along with a somewhat higher content of microcrystalline quartz (40 %). This may be attributed to the smectite decomposition which takes place during the sediment burial, resulting with the release of silica (BLATT, 1979). The inverse correlation of the quartz and smectite component in illite-smectite is particularly indicative in that regard. The X-ray diffraction on clay fraction (<2 μm) revealed illite and several generations of illite-smectite, including rectorite, as dominant clay phases. The mineralogy of smaller fraction (<0.5 μm) showed, however, a comparatively higher smectite content in mixed layers, thus pointing to the smectitic precursor of these diagenetic products. More work is envisaged to fully understand how diagenesis operated in the studied Pennsylvanian strata. This includes the transmission and scanning electron microscopy on selected samples as well as K-Ar dating and chemical analyses of different sediment fractions (<2 μm). The preliminary trace element study on a 150 m long core of Pennsylvanian shaly sediments from the Anadarko Basin is especially illustrative, showing consistent values of normalized concentrations of selected trace elements. Yet, the facies of black shales portray trace element abundances that are higher in magnitude by several orders, which is correlative with the composition of illite-smectite intermediates.

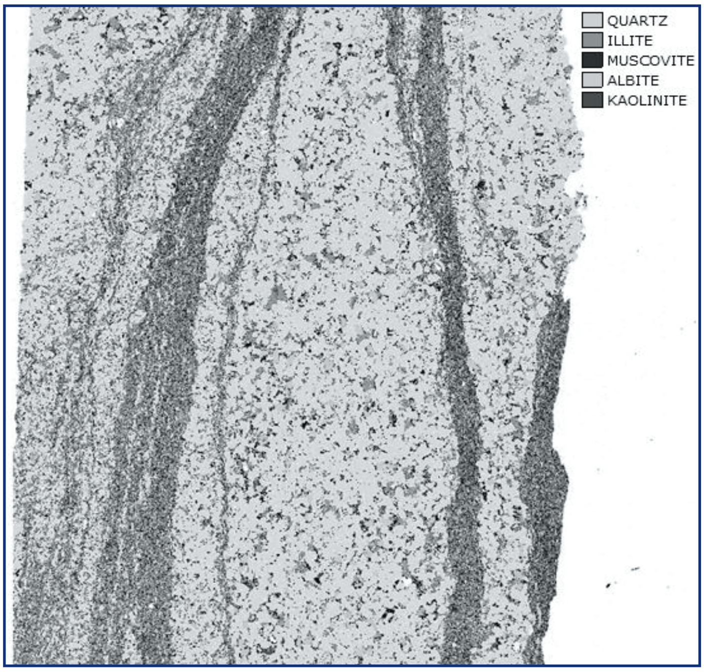

Figure 1. Example of clastic rocks from the Pennsylvanian Hoxbar Group (Anadarko Basin, Oklahoma). Qemscan image, width = 10 cm.

Very promising first results and comprehensive analytical approach envisaged, along with the sampling strategy that seek to cover a large vertical sediment surely span of approximately 2 km (the Hoxbar, Atokan and Virgilian shales for the Anadarko Basin), will surely add to our understanding of the origin of Late Paleozoic shales that are found across the major sedimentary basins of the American Midcontinent.

Acknowledgments

This study is supported by Texas Tech University and several smaller research grants provided by the American Association of Petroleum Geologists (AAPG).

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Quantitative analysis of clay minerals and poorly ordered phases by prior determined X-ray diffraction full pattern fitting: procedures and prospects

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It has long been recognised that many of the properties of materials such as soils, industrial clays, and shales depend in many ways on the contents and character of the clay minerals and other poorly ordered phases which they may contain. Quantitative phase analyses of these materials are therefore desirable in many cases. However, clays and poorly ordered phases are amongst the most difficult of any phases to analyse quantitatively and this is reflected by the almost continuous effort since the first application of X-ray diffraction to clay materials to develop and refine new methods of quantitative clay mineral analyse. In recent years, full pattern approaches based on the Rietveld method have proved very popular, probably because of the success of this approach with more conventional well-ordered minerals and also the increasing availability of Rietveld codes. Nonetheless, due to the disordered nature of most clays the application of the Rietveld method to clay materials remains a challenging undertaking. A simple alternative that captures the power of the full pattern approach is to use predetermined patterns (measured or calculated). The basic premise of this pattern fitting method is that a diffraction pattern of a mixture of minerals can be simulated as a weighted sum of the diffraction patterns of its components. In essence, this approach is like the Rietveld approach but without the refinement and solution of anything other than the proportions of the patterns required to model the unknown. One additional benefit of using measured patterns is that the background can be included as data and this is especially useful when dealing with X-ray amorphous or poorly ordered phases which can be quantified directly. There are various implementations of pattern summation methods but the underlying principles that relate pattern proportions to quantitative mineral proportions are all fundamentally based on the concept of a reference intensity ratio (RIR). Pattern summation methods are relatively easy to implement and do not require the level of crystallographic understanding for mastery of the Rietveld approach. They also do not require the addition of an internal standard. Their main drawback is the time and effort required to set up a library of appropriate calibrated pure mineral, disordered phase, and amorphous patterns. The procedures and capabilities of the prior determined full pattern fitting method will be illustrated by its application to a diverse set of soil, industrial clay and shale samples. Future prospects are directed towards library calibration routines to make them more widely applicable and towards high throughput procedures which seek to couple clay mineral identification with quantification.

About relations of properties and performances of bentonites

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Clay scientists are trying to understand the reasons for the different performances, e.g. different swelling capacities, of bentonites. A suite of different methods exist for the characterization of bentonites which differ with respect to mineralogical composition (smectite content, type and amount of admixtures), chemical composition of smectite, layer charge density (distribution), primary particle size (distribution), particle morphology, microstructure (relative arrangement of particles to each other), micro- and mesporosity, and type of exchangeable cation. All these parameters may affect the performance of bentonites in different applications ranging from wet-based applications (drilling mud, paper making, paint additive, adsorber,…) to dry systems (foundry, pelletizing, animal litter, barriers,…). Some relations of properties and performance are well established as the effect of different types of exchangeable cations (Na or Ca) on swelling and rheology or the Fe-content on the thermal stability in foundry or ceramic applications.

The type of exchangeable cation affects the cation/water arrangement in the interlayer which is the dominant surface of smectites and hence particularly important. With excess water Na-smectites tend to delaminate forming soft gels or at larger water contents stable suspensions while Ca-smectites remain as quasicrystals in a 3–4 water layer state. Even present in low amounts the soft Na-smectite gels can effectively seal porous rocks but at the same time the probability for detachment of colloidal particles from soft gels is larger compared to Ca-smectites (KAUFHOLD & DOHRMANN, 2008).

The layer charge density (LCD) of the smectites determines the CEC and is supposed to affect the bentonite performance, particularly with respect to swelling, coagulation, and adsorption. Swelling of different bentonites was measured both in an unconfined (free swelling) and in a confined system (swelling pressure). The free swelling volume depends mostly on the amount of exchangeable Na^+ as the swelling pressure in the confined system at low dry densities. At larger dry densities the microstructure was found to affect the dry density / swelling pressure relation. The micro- and mesoporous samples B14 and B32 both showed much larger swelling pressure compared with the dry density than other bentonites (KAUFHOLD et al., 2015a). This can at least partly be explained by the higher porosity of both samples which is not reduced upon compaction. This uncompactable porosity rather than layer charge density determines the swelling pressure at a given dry density. The effect of layer charge density on the swelling properties is often reported and discussed but difficult to prove. On the other hand a clear correlation was found between the LCD and the corrosivity of bentonites in contact with metal iron (anaerobic and heated; KAUFHOLD et al., 2015b). This can probably be explained by a different redox potential of smectites depending on the layer charge density. Smectites with higher LCD are less corrosive probably because their structural Fe^{3+} is less readily reduced by anaerobically produced H_2 as that of low charged smectites. In addition, the layer charge density is supposed to affect the amount of fixed cations of smectites. Six pure smectite samples were investigated with respect to their chemical composition after exchange for Cu-trien and alkylammonium, respectively, which exchanged all exchangeable cations (KAUFHOLD et al., 2011). Still, however, some Na_2O, CaO, and K_2O were found in the samples. The sum of these elements apparently depended on the LCD which in turn led to a possible explanation for the systematic difference of LCD values determined either by AAM (LAGALY, 1994) or by the structural formula method (SFM). According to this model the latter would represent all interlayer cations, exchangeable and fixed cations, and methods based on the cation exchange, as AAM, can only probe the amount of charges which are saturated by exchangeable rather than fixed cations. This model, however, still has to be validated.

The amount of tetrahedral charges was found to affect the critical coagulation concentration and hence the stability of dispersions as already stated by FREY & LAGALY (1979). The extraordinary stability of Wyoming bentonite dispersions against salt solutions, however, cannot be explained based on the tetrahedral charge only (KAUFHOLD et al., 2018).

In the lecture more examples for apparent relations of properties and performance of bentonites will be presented, such as the effect of soda soluble silica on rheological and chemical stability of smectite in cement mixtures (OHRDORF et al., 2011).

Despite the identification of some interesting new correlations, bentonite performance in different applications can still not be predicted based on material properties.

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Paleoenvironmental and paleoclimatological assessment of the Kalecik basin based on multi-proxy data from the lake sediments of the Neogene Hançılı Formation, Central Turkey

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Lake deposits with their mineralogical and geochemical composition, faunal and floral assemblages and other proxies are important to understand the past climates. Since lakes accumulate materials transported from their surrounding region they also provide a record of environmental changes (BRADLEY, 1999; AZIZ et al., 2003).

In this study, the mineralogical, geochemical and stable isotopic characteristics of a total of 51 samples collected along the two stratigraphic sections in Koyunbaba village and Höyüklü Hill and an additional 60 m deep borehole (SSK-1) at Tepetarla location in the Kalecik lake basin were investigated to assess paleoenvironmental and paleoclimatologic evolution of the Neogene Kalecik Basin. Petrographic investigation of thin-sections, XRD, SEM-EDX, XRF and stable isotope analyses (15 samples) were performed to determine the mineralogical and chemical compositions of the samples. The presence of authigenic analcime and dolomite, detrital chlorite and illite, together with K_2O/TiO_2, MnO/Al_2O_3, Na_2O/Al_2O_3, Na_2O/TiO_2, Na_2O/K_2O, Al_2O_3/K_2O, $MgO/(MgO+CaO)$, and Ba/Sr ratios as well as $\delta^{18}O$ and $\delta^{13}C$ isotope ratios were applied to evaluate the paleoclimatic responses recorded by lacustrine sediments of the Hançılı Formation, which is characterized by marl, limestone, bentonitic claystone, mudstone and sandstone intercalated with andesitic tuffs and andesites.

The results point out that humid periods favored intense leaching which resulted in changes of the mineralogical and geochemical input to the lacustrine basin. The following arid periods correspond to dry, saline and alkaline conditions. Additionally, the $\delta^{18}O$ values between -2.32 ‰ and -8.77 ‰ VPDB suggest influence of meteoric water; while the $\delta^{13}C$ compositions range from -3.85 ‰ to -7.63 ‰ VPDB favouring C4 paleo-vegetation. Obtained results show that the study area experienced mostly dry periods associated with saline-alkaline conditions during Middle Miocene to Early Pliocene, time period which the age of the Hançılı Formation corresponds, based on the pollen assemblage from coal seams, some vertebrate fossils (KOÇYİĞİT et al.,1995) and evolution of dentition of murid-genera (KAYMAKÇI et al., 2001). The isotope values are consistant with the warm periods of Middle Miocene Climatic Optimum.

Acknowledgements
This study was financially supported by TÜBİTAK project No:101Y130.

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International Bentonite Longevity (IBL) project: an overview

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Kunimine Industries Company's (KIC) Tsukinuno bentonite mine (NW Japan) is a source of Miocene age Na- (at depth) and Ca- (near surface) bentonite (e.g. TAGAKI, 2005). The site holds great potential for studying processes of direct relevance to safety cases (SC) for radioactive waste repositories which will utilise bentonite as part of their multi-barrier safety system.

The mine and its environs are ideal for studying long-term, safety-relevant bentonite processes, including (see REIJONEN et al., 2018a, for details):

- *saturation state* – natural saturation states of bentonite in differing environments (on the surface and at varying depths underground, dry and wet host rock conditions) for comparison with ongoing short-term, laboratory and underground rock laboratory (URL) tests
- *bentonite density changes* (swelling and heave) - due to exposure to groundwaters/meteoric waters
- *bentonite water interaction processes with fresh and deeper groundwater chemistries* – for example, changes in cation exchange capacity (CEC) and exchangeable cation composition (EC)
- *bentonite erosion* – both under repository-relevant conditions at depth in the tunnels where water conducting features contact the bentonite and under extreme conditions (river erosion at the surface)
- *bentonite reaction* - with mudstone and siltstone host rocks (of relevance to borehole seals)
- *bentonite sampling and analytical development* – novel sampling (see discussion in EWY, 2015; ALEXANDER et al., 2017) and analytical (REIJONEN et al., 2018b) approaches for a bentonite research project will be explored.

As such, the 31 bentonite layers in the Tsukinuno mine, varying in thickness from a few cm to ca. 7 m, will provide relevant information to the long-term behaviour of bentonite in a repository for radioactive waste. This includes both physical and temporal scales appropriate to the buffer and backfill clays to be utilised in the repository multi-barrier safety system. The IBL project has just started (first field campaign completed, analysis underway) and this presentation will provide an overview of the ongoing and planned work in the project.

Acknowledgements
With many thanks to KIC for their enthusiastic support, to GTK for the presented analyses and to Dr G. Kamei (JAEA, Japan) for his help in initiating the IBL project.

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Shear strength anisotropy of clays from Bedekovčina region in Croatia

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Nowadays, in the time of rapid development, it is often impossible to choose a desired location to build large and complex structures that are therefore built in very complex geotechnical conditions. In Civil Engineering, clay soil is considered a complex engineering geotechnical environment. For instance, construction works carried out in a clay environment include constructing clay pits, underground structures, subways, underground parking lots, foundations, etc. In the process of designing these structures, it is necessary to determine the parameters of the shear strength characteristics of the clay soil from which, according to known theoretical models, one can calculate the bearing capacity of the soil, the pressure of surrounding soil on the structure, the stability of the clay mass (the limit state of stress), i.e. determine the load on the structure, which is crucial for dimensioning. The clay shear strength parameters are usually quantified by the Mohr-Coulomb model, using two parameters - internal friction angle - φ and cohesion c. For their determination, in accordance with the norms and regulations, the most commonly used (MAKSIMOVIĆ, 2008) test is the direct shear test.

The complex structure, texture, and discrete nature of clay makes clay behave differently in different directions, due to anisotropy of its physical characteristics (SHKOLA, 2012; EWERTOWSKA-MADEJ, 1972), greatly affecting the parameters of shear strength and consequently affecting the dimensioning of objects and the stability of clay soil mass.

In the presented paper, the anisotropy of the shear strength of the clay samples from the "Đurđevičev Breg" clay pit in Bedekovčina was investigated. Direct shear tests of 27 clay samples (9 series of tests) from the clay pit were conducted. The clay samples were taken in different directions relative to the horizontal plane, 9 samples in each of three directions - 0°, 45° and 90° relative to a horizontal line. In addition, standard sample tests on clay samples were performed, testing unit weight, water content, liquid and plastic limits. As a result, anisotropic hodographs of shear failure parameters are obtained, demonstrating that the anisotropy of the yield strength is considerable and needs to be taken into account in the calculation of a limit stress state. In the work of SHKOLA (2010) based on numerous investigations and theoretical models of anisotropic soils, taking into account the anisotropy of shear strength in limit stress state calculations when there's a difference in an angle of internal friction larger than 5 % and in a cohesion c more than 10 % is recommended.

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Effect of talc, huntite, and magnesitic clay and sepiolitic–dolomite additions as different MgO sources on physical properties of Ca-rich ceramic bodies

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The effect of Mg-minerals such as talc, huntite, magnesitic-clay and sepiolitic–dolomite on the physical properties of green and fired clay-based Ca-ceramic bodies was investigated. The physical properties of clay-based ceramics are important to their performance and also provide a useful, quantitative estimate of quality. In this study, Ca-Mg clay-based ceramic bodies were prepared using calcite and four different Mg minerals; 15 % calcite was added in addition to 5 % of one of the Mg-minerals (talc, huntite, magnesitic clay or sepiolitic–dolomite clay). The used calcite percentage was consistent with previous studies which reported that the content of CaO in the ceramic body should be 5–15 wt% (DONDI, 1999) or 5–10 wt% (PETERS & IBERG, 1978) for maximum anorthite formation.

The 5 wt% Mg-minerals additions to the Ca- bodies, except for huntite, have improved their strength. The bending strength of ceramic bodies with addition of 5 wt% talc, 5 wt% huntite 5 wt% sep-dol and 15 wt% calcite bodies were 366 kg/cm^2, 231 kg/cm^2 400 kg/cm^2 and 244 kg/cm^2 respectively at 1250°C.

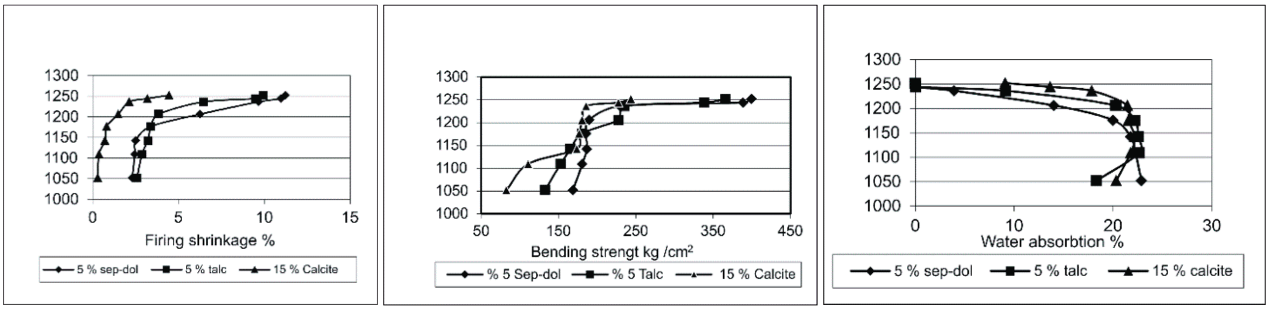

Figure 1. Effect of 5 wt% Mg flux on bending strength, firing shrinkage and water absorption as a function of firing temperature.

The temperatures of 1150°C, 1200°C and 1250°C are critical for physical properites and can be easily determined from the bending points of the curves shown in the graphs of firing shrinkage, water absorption and bending strength of ceramic bodies after addition of sepiolitic-dolomite, talc and calcite (Fig. 1).

This improvement is not only due to the 5 wt% Mg-flux additions which enhance anorthite formation and widen stability range of anorthite, but it is also controlled by chemical compositions of individual Mg flux additions (ARAS, 2018). Except for talc, all ceramic bodies contain carbonate; however high strength is measured in the sepiolitic-dolomite body, not in the talc body, although talc is the most convenient additive in preventing porosity formation. It is probably possible to explain this behaviour with the low porosity measured in the green sepiolitic-dolomite body versus the high primary porosity (i.e., high open porosity or water absorption) measured in the green talc-body (Fig. 1). The formation and wide stability range of anorthite as well as the chemical composition of Mg additions is important in improving the E modulus and bending strength of clay based bodies even with small amounts of 5 wt% Mg flux additions and 15 % calcite.

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Influence of quaternary alkylphosphonium and alkylammonium cations on the interaction of synthetic saponite with laser dye

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Various types of cationic surfactants have been used for the preparation of organically-modified clay minerals. Such materials have further been used for the preparation of hybrids with laser dyes. Systems based on smectites modified with alkylammonium cations have shown to be effective in preventing dye aggregation, a phenomenon that reduces dye luminescence (e.g. SASAI et al., 2009). With the exception of frequently used alkylammonium ions, alkylphosphonium cations have recently been examined for the preparation of organoclays, mainly because of their higher thermal stability, which is important for the preparation of polymer nanocomposites. The aim of this work was to study the effect of organic cations on the final properties of organoclays and to investigate the interactions within hybrid systems with laser dye rhodamine 6G (R6G) by means of XRD and IR spectroscopy.

Synthetic saponite Sumecton (Sap) was modified with tetraoctylphosphonium (TOP) and tetraoctylammonium (TOA) cations in amounts equal to 25, 50, 75, 100 % of the cation exchange capacity (CEC). Furthermore, another series of samples with R6G was prepared with the R6G/Sap ratio 0.02 and 0.1 mmol/g and variable amounts of the organic surfactants. Carbon content showed a substantial increase with the amount of surfactants. The intercalation of organic cations caused an expansion of the interlayer spaces from 1.2 nm (detected for a pure Sap) up to 2.1 and 2.2 nm for 100 % TOA- or 100 % TOP-Sap, respectively. Higher d_{001} within the TOP-Sap series could be attributed to the larger P atom radius compared to the N atom. The addition of R6G to Sap caused a visible change in d_{001} for both tested dye concentrations, while for the systems based on organoclays, the interlayer space remained more or less unchanged. Based on carbon content values, organoclays adsorbed less R6G than pure Sap.

IR spectra in the middle (MIR) and near infrared (NIR) regions were measured to follow the influence of the organic cations on the shape of the spectra. TOP- and TOA-salts showed distinctive spectral profiles of C-H bands due to different central atoms of surfactant head-groups that affected the neighbouring bonds of methylene groups, thus also the frequencies and intensities of IR bands. Upon loading of both cations to Sap layers, the bands attributed to the C-H vibrations of methyl and methylene groups appeared in the spectra: stretching νC-H between 3000–2800 cm^{-1} and bending δC-H within 1600–1300 cm^{-1}. The shapes of the C-H bands were modified compared to the pure organic salts spectra. The most intensive bands detected in the salts became less resolved, but the spectral differences between the two organic surfactants were also transferred into spectra of organoclays. The areas of organic cation absorption bands were evaluated for the spectra normalised to νSi-O band of Sap. Both TOP-Sap and TOA-Sap showed an enlargement in the band areas of νC-H and δC-H with increasing carbon content. The intercalation of R6G in the samples was clearly confirmed by the appearance of sharp bands attributed to δC-H and to vibrations of aromatic rings between wavenumbers 1700–1300 cm^{-1}. These bands did not overlapped with wavenumber of δC-H bands of the surfactant cations, thus they were also observable in the spectra of TOP-Sap and TOA-Sap samples modified with R6G. Their intensity increased with the concentration of R6G.

NIR spectra of TOP-Sap and TOA-Sap provided complementary information to that obtained from the MIR spectra. In addition to the first overtones (2ν) and combination vibrations (ν+δ) of structural OH of Sap (7186 and 4321 cm^{-1}) and of water molecules (6834 and 5258 cm^{-1}), the NIR spectra also showed a complex band in the 6000–5400 cm^{-1} region related to the 2νCH vibrations, and (ν+δ)CH vibrations detected below 4500 cm^{-1}. The enhancement of hydrophobicity of 100 % TOP-Sap and 100 % TOA-Sap was confirmed by a significant drop in the intensities of $2\nu H_2O$ and $(\nu+\delta)\ H_2O$ bands. NIR spectroscopy displayed only negligible changes in the spectra after modification with R6G, although a sufficient amount of the dye was distinguished by carbon analysis in R6G-Sap and although the dye was clearly detectable in MIR spectra of all measured samples. The appearance of an unidentified band at 6748 cm^{-1} that was not visible in the pure R6G spectrum, could be attributed to the interactions of dye cations with Sap and its organic derivatives.

Acknowledgments

The authors gratefully acknowledge financial support from the Slovak Grant Agency VEGA (project No. 2/0132/13), Slovak Research and Development Agency (projects Nos. APVV-15-0741 and APVV-15-0347).

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Study of iontophoresis process using clays as a transdermal drug delivery system

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Clays have been used empirically for therapeutic purposes since ancient times, through ingestion (geophagy) or topical application in the form of cataplasms or mud baths, known as pelotherapy. Transdermal drug delivery (TDD) is considered an effective and innovative method for delivering drugs through the skin. The process consists of passing a drug through the skin barrier, *stratum corneum*, then the *epidermis* and *dermis* into the bloodstream to be transported to the site where it is expected to achieve therapeutic effects. The passage of therapeutic amounts of substances or drugs through the skin and into the bloodstream allows therapeutic effects to be obtained quickly. However, the skin is still a barrier. Iontophoresis is a non-invasive electrotherapy method for the transdermal application of drugs, facilitating the transfer of ionic substances through the skin barrier using low intensity electric current.

An innovative “electropelotherapy” device prototype was developed, according to the specifications of a non-invasive medical device that ensures the transdermal transmission of the active principles of clays. After a Phase I - clinical trial for safety dosage validation, different studies were performed to study the technological properties of clays (commercial and maturated in lab) and to assess the impact of electric current and temperature on a selected peloid. The present study aims: 1) to analyse the physical, chemical and mineralogical characterisation of lab maturated clays in controlled conditions and compare these with some clayey commercial products available on the market; 2) to observe the electric and thermal behaviour of a selected peloid when subjected to a controlled dose of electric current and temperature.

Several analyses were carried out, namely: mineralogical (X-ray diffraction), geochemical (major and minor elements) analyses (X-ray fluorescence), abrasiveness, plasticity, cation exchange capacity and exchangeable cations, specific surface area, expandability, oil absorption and cooling rate.

The results obtained so far show that almost all the samples are mainly siliciclastic (a few carbonated), with kaolinite or illite as principal clay minerals, and smectite as a minor component. In general, samples present a chemical composition compatible with the desired applications, Ca being the main exchangeable cation, followed by Mg or Na. Regarding technological properties, more siliciclastic samples richer in clay minerals revealed lower abrasiveness, higher expandability and cooling kinetics. It was also demonstrated that higher ionic mobility is observed when the intensity of the galvanic current is higher than 5 mA and the peloid has a temperature higher than 40ºC.

Acknowledgments

This study was financed by the Portuguese Foundation for Science and Technology (FCT) and Exatronic, Lda. (PhD grant SFRH/BDE/11062/2015, for the first author) and also supported by GeoBioTec Research Centre (UID/GEO/04035/2013), funded by FCT.

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Removal of spiramycin from aqueous solutions using natural and purified Algerian palygorskite

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Natural (Sif Pal) and purified palygorskites (Pur Pal) were used for studying the adsorption of an antibiotic (spiramycin) worldwide consumed. Both palygorskites have been characterized by infrared spectroscopy, X-ray fluorescence analysis, X-ray diffraction, N_2-BET and electron microscopy (TEM) (BELAROUI et al., 2014; OUALI et al., 2015). The average mineralogical formula of Pur Pal is as follows: $(Si_{7.88}Al_{0.12})\ O_{20}\ (Mg_{1.69}\ Al_{1.71}\ Fe_{0.43})\ (OH)_2\ (K_{0.06}\ Ca_{0.05}\ Na_{0.15})\ (OH_2)_4{\times}4H_2O$ (BELAROUI et al., 2018). An adsorption study was carried out to evaluate the potential of these palygorskites to retain spiramycin from polluted water. Different parameters were evaluated such as the mass of the clay, the effect of pH or the concentration of spiramycin in solution. The concentration of spiramycin was determined by ultraviolet spectrophotometry. Kinetic and adsorption experimental data were fitted to different models. The removal efficiency of spiramycin was higher with Pur Pal (89.2 %) than with Sif Pal (73.6 %). The adsorption kinetics of the antibiotic was better fitted to a pseudo-second order model. Regarding the adsorption process, the Langmuir and Temkin equations explained better than Freundlich the adsorption of spiramycin on Sif and Pur Pal, with a maximum adsorption capacity of 10.2 mg g^{-1} for Pur Pal, doubling that of Sif Pal (Fig. 1). The Algerian palygorskite could be used as a cheap alternative for the removal of spiramycin from wastewater.

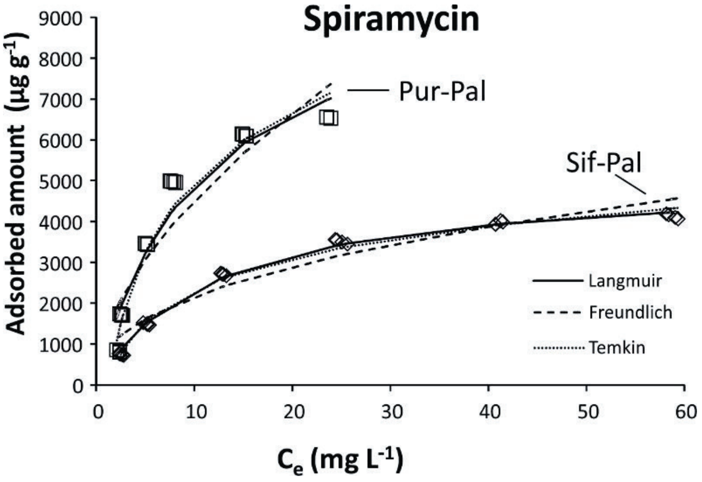

Figure 1. Adsorption isotherms of spiramycin on Sif Pal and Pur Pal and fitting to different models.

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Russian bentonite clay deposits: geological occurrences, structure and properties

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Bentonite clays are important materials widely used in many sectors of industry. However, the quality of raw materials, their properties and reserves directly depend on the conditions of its formation, namely the geological-tectonic, geochemical and paleo-facial environments.

The estimated reserves of bentonite clays in Russia are about 157 million tons (A+B+C_1-grade) and additional 83 in category C_2 (BELOUSOV et al., 2017). Currently the most important bentonite deposits are Biklyanskoe and Berezovskoe with explored reserves of 38.7 million tons (Republic of Tatarstan), Ziryanskoe with explored reserves of 14.4 million tons (Kurgan region) and “10th Khutor” with explored reserves of 4 million tons (Republic of Khakassia).

The classification of bentonite clays by their origin is a debatable issue. Deposits of bentonite clay are divided into following groups: volcanic-sedimentary (devitrification of volcanic ash in slightly alkaline waters); hydrothermal (hydrothermal transformation of volcanic and sedimentary rocks); sedimentary (redeposited clay); eluvial (weathering crust). The main bentonite types presented in Russia are sedimentary and volcanic-sedimentary ones.

Sedimentary deposits are usually characterized by a simple geological structure, large reserves and poor quality of bentonite. Montmorillonite content ranges from 40 to 70 %. The largest Russian bentonite deposits belong to this type and are located in the Republic of Tatarstan, Omsk region and Orenburg region. Bentonites of volcanic-sedimentary type are of high quality and have complicated geological structure. Montmorillonite content ranges from 50 to 80 % (both alkaline and alkaline-earth type). The deposits of bentonite clays of volcanic-sedimentary type are located in Republic of Khakassia with reserves of 6 million tons and Sakhalin Island with total reserves of about 4 million tons.

An important feature of volcanic-sedimentary deposits is the formation of bentonite provinces, associated with coal basins. The relationship between bentonite clays and coal deposits is explained by the fact that conditions of sedimentation of fossil coals are favorable for the formation of bentonites from volcanic ash. There are two main conditions that should be met for formation of bentonite-bearing provinces: acid volcanism in the region, and wide distribution of coal basins.

To study the structure and properties of bentonite clays from the most promising and large deposits of Russia and nearest CIF countries for using as buffer barriers in the disposal of radioactive wastes, the following methods were used (KRUPSKAYA et al., 2017): XRD, FTIR, DSC/TG, S_{BET} and CEC estimation and others. One of the important directions of the study was sorption of Cs and Sr, including radionuclides, on natural bentonite clays.

Table 1. Basic properties of bentonites from studied deposits.

Deposit	Smectite content*, %	CEC**, meq/100g	BET, m^2/g	Swelling index, mL/2g	A_{max} (Cs)***, meq/100 g	A_{max} (Sr), meq/100 g
10th Khutor	73	37 - 80	13	4	67	80
Ziryanskoe	74	27 - 78	45	4	55	81
Dashkovskoe	57	49 - 68	64	6	63	63
Dinozavrovoe	73	82 - 101	110	19	104	105
Dash-Salakhly	74	80 - 94	67	35	Not measured	Not measured

Location of the deposits: Russia- 10th Khutor, Dashkovskoe, Ziryanskoe; CIF – Dinozavrovoe (Rep. Kazakhstan), Dash-Salakhly (Rep. Azerbaijan)
* - montmorillonite content was estimated by the XRD (Rietveld method), ** - CEC measurements were done by methylene blue method and triethylenetetramine copper complex (MB/$[Cu(Trien)]^{2+}$), *** - Value of max. adsorption in relation to cesium / strontium.

Acknowledgments
This work was financially supported by the Russian Science Foundation (Project #16-17-10270).

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Characterization of bacteria in nickel-rich kaolinite, montmorillonite, and saponite mixture from Gornje Orešje, Croatia

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A sample of nickel (Ni)-rich clay from Gornje Orešje (POSILOVIĆ, 2009), Croatia was analysed mineralogically and bacteriologically. The light greyish-green sample of alteration product of peridotite mother rocks was recognized as a mixture of kaolinite, montmorillonite, saponite and negligible quantity of quartz and calcite. The abundance of total heterotrophic bacteria grown at 22°C was 7.0±0.8 log colony-forming unit (CFU)/mL of wet clay. The population of carbapenem-resistant bacteria grown at 35°C was present at abundance of 3.9±0.6 log CFU/mL. According to the Bruker MALDI-TOF MS analysis, the population of carbapenem-resistant bacteria was represented by *Stenotrophomonas* sp. with intrinsic resistance, and *Pseudomonas* sp. with acquired resistance to carbapenems.

The results suggest that Ni-rich clay is a habitat of dense bacterial population, including those resistant to last-resort antibiotics. Scanning Electron Microscopy analysis (Fig. 1) confirmed that bacteria were mostly restricted to the edges of montmorillonite sheets, which probably represent the sites of easy access of bacteria to the cations present in mineral.

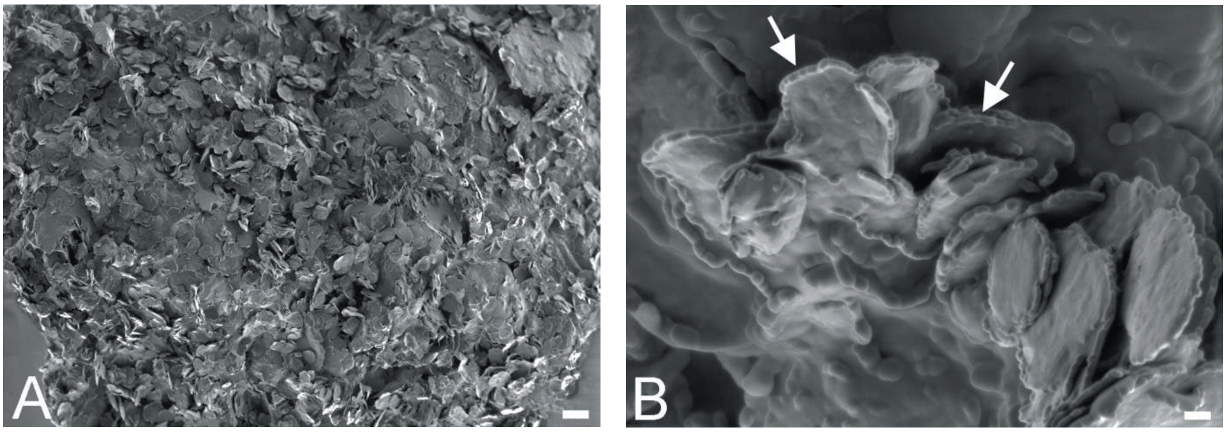

Figure 1. Scanning electron microscope micrographs of the Ni-rich clay (A) and the population of bacteria (arrows) that was mostly restricted to the edges of montmorillonite sheets (B). Scale bars: A: 2 µm and B: 200 nm.

Acknowledgements
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Biogeochemical characterization of sediments under the anthropogenic influence at mouth of Rio de Minas, Punta Arenas, Chile

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Lack of purification of urban wastewaters before its discharge to the natural recipient could represent the epidemiological route for spread of pathogenic bacteria. Currently bacteria resistant to carbapenems have become a worldwide problem (MELETIS, 2016).

Three sediment samples were collected during autumn at the mouth of Rio de Minas in Punta Arenas, Chile, South America: two from river flow and one from the Pacific sea. Fine river sediments (sand to silt) were dark brown to black in color, without any smell. X-ray diffraction allowed the identification of mixture of montmorillonite and kaolinite with quartz and albite, while ilmenite was also identified in one sample.

Heterotrophic bacteria were found in abundance of 6.2-6.6 log colony-forming unit (CFU)/mL in all three sediment samples. We also found as much as 1.9 and 2.7 log CFU/g of carbapenem-resistant bacteria in river sediments, but they were absent in seawater sediment. The prevalence of carbapenem-resistant bacteria among total heterotrophic bacteria was 29 % and 42 % log CFU. The results are comparable to the prevalence of carbapenem-resistant bacteria (49 % log CFU) reported in landfill leachate (DURN et al., 2014). As confirmed by Bruker MALDI-TOF MS analysis, the carbapenem-resistant bacteria were represented by species of the genus *Pseudomonas*, which are acquired resistant to carbapenems. Scanning Electron Microscopy confirmed the presence of randomly distributed bacteria (Fig. 1) in the sediment samples.

The river sediments under anthropogenic influence of untreated urban and technological wastewaters reveal a significant source of potentially pathogenic carbapenem-resistant bacteria.

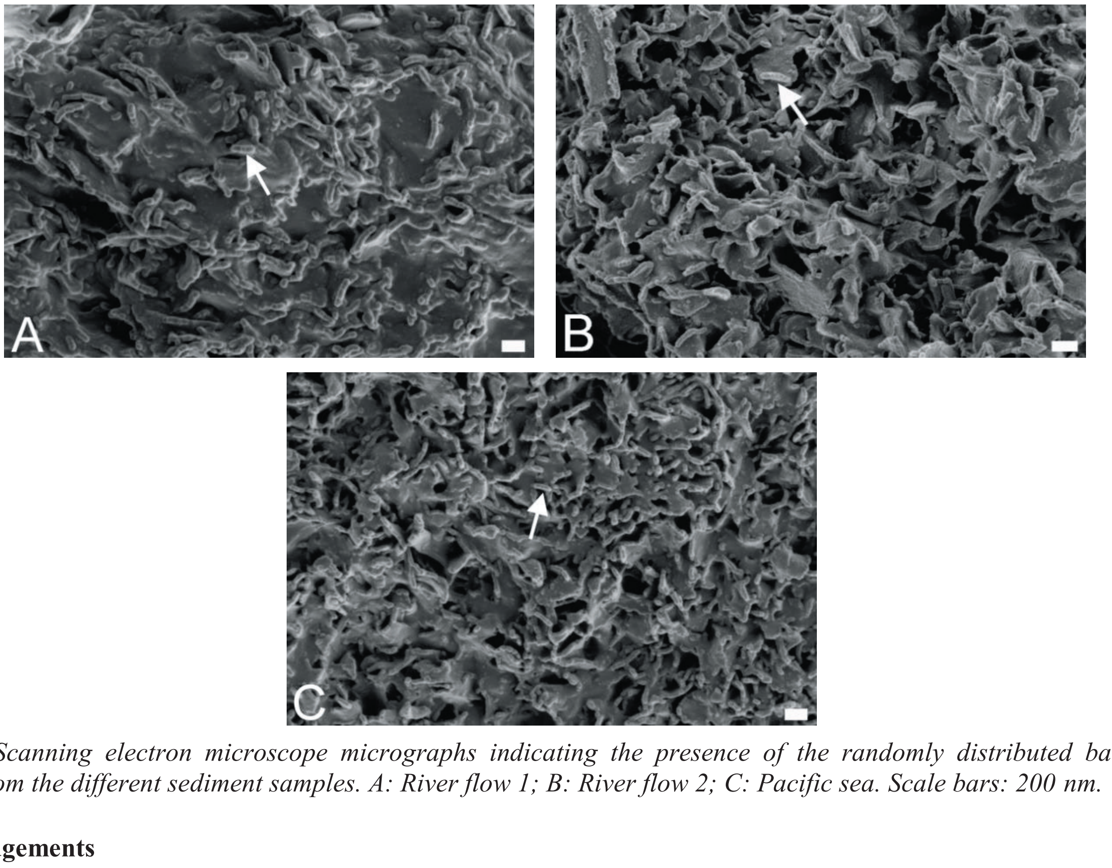

Figure 1. Scanning electron microscope micrographs indicating the presence of the randomly distributed bacteria (arrows) from the different sediment samples. A: River flow 1; B: River flow 2; C: Pacific sea. Scale bars: 200 nm.

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Sorption of Ni^{2+} and Zn^{2+} on selected natural and synthetic materials

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Heavy metal pollution represents a serious problem for the environment. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. The adsorption and ion exchange method appears to be the most widely used for the removal of heavy metals (EL-ESWED et al., 2012). Cheap, readily available and effective materials, such as Mn oxides, clay minerals, natural zeolites, or zeolites synthesized from Si and Al-rich waste materials are suitable for the removal of heavy metals from the environment. Bentonites and zeolites are suitable for the removal of heavy metal cations from the environment due to the negative charge of their structure. Negative charge is compensated with alkali and alkaline earth metal cations that are readily exchangeable with heavy metal cations from the environment. The cationic exchange capacity of bentonite is between 0.8 – 1.5 meq/g (LA GREGA et al., 1994), while zeolites can reach up to 7 meq/g (BASALDELLA et al., 2007). While main sorption mechanism in bentonites and zeolites is ion exchange, adsorption is the main process in Mn oxides. Mn oxides are usually applied on the soil, where they form strong complexes with metals, due to negative charge of their structure. An important property of Mn oxides is their ability to oxidize and reduce elements. This work is aimed on comparison of sorption properties of materials such as bentonites, natural and synthetic zeolites and Mn oxides for the sorption of ions of selected heavy metals - Ni^{2+} and Zn^{2+}. We will compare the efficiency of heavy metal sorption on different sorbents at different pH and at different concentrations of heavy metal ions in the solutions. Besides single element solutions, natural waters that have been contaminated with heavy metals due to historical mining activities will be used as well. In the experiments bentonite SAz-1 (montmorillonite, Arizona, USA), natural zeolite rich in clinoptilolite (Nižný Hrabovec, Slovakia), commercial synthetic zeolite 13X and synthetic amorphous Mn oxides (AMO) prepared according to DELLA PUPPA et al. (2013) will be used. Zeolitic materials containing variable amount of zeolites X, P, sodalite, phillipsite, analcime and cancrinite, synthesized from the fine perlite by-product material from Lehôtka pod Brehmi will be also tested. Stock Ni and Zn solutions (1 g/L) were prepared by dissolving $NiCl_2$ and $ZnCl_2$ in deionized water. The solid/liquid ratio in all experiments will be 100 mg to 10 ml. Reaction time will be determined by the results of kinetic experiments. Heavy metal concentrations for batch adsorption experiments will range from 0.1 to 100 mg/L. Adsorption experiments will be also performed at constant concentration and different pH values. The experiments will be performed in an orbital shaker. The samples will be then analyzed by ICP-OES. Zeolite 13X is expected to be the most efficient of all sorbents, due to high CEC and purity of synthesized material. Although zeolites synthesized from perlite may possess high CEC as well, their drawback lies in the variable composition. These samples consist of several zeolites, unaltered volcanic glass and accessory minerals. Presence of these non-zeolitic components results in lower ion exchange capacity, thus sorption of synthesized zeolites is decreased. Efficiency of sorption depends also on zeolite types present in the sample. While samples containing zeolite X should be the most efficient sorbents, samples rich in sodalite and cancrinite are expected to show low sorption efficiency. Sorption efficiency of samples containing zeolite P, phillipsite and analcime should be comparable with bentonite sample. Since ion exchange properties of Mn oxides are significantly lower than those of bentonites and zeolites, sorption mechanism will be based mostly on adsorption, thus lower sorption efficiency is expected.

Acknowledgments
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Near-infrared spectroscopy: the useful tool for monitoring the conformations of organic cations during hydration and dehydration

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The modification of montmorillonites (Mt) with cationic surfactants is an important subject of current research since various organoclays are widely used in different industrial and environmental applications. Understanding the microstructure of organo-montmorillonites under wet/dry conditions is of high importance in clarifying their adsorption characteristics towards hydrophobic organic compounds in water. The objective of the present study was to examine the arrangement of dioctylammonium cations (2C8) within the Mt interlayers at different organic cation concentration, water content and temperature. The Mt from Jelšový Potok, Slovakia (JP) and 2C8-Br in loading concentration range of 0.2–2.0 mmolg^{-1} (corresponding to 20–200 % of the CEC of JP) were used for organoclays preparation. Carbon analysis, XRD, and near-infraed (NIR) spectroscopy were used for the samples characterization. The highest degree of the surfactant adsorption, calculated from measured carbon content, was 172 % of CEC. It is assumed that in addition to 2C8 cations the organic salt was co-adsorbed to Mt interlayers and/or outer surfaces. The d_{001} value of 2C8-JP showed consecutice creation of monolayers, bilayers and paraffin arrangement. The complex band near 5800 cm^{-1} related to the first overtone of CH groups ($2\nu_{CH}$) was used to probe the ordering of the intercalated cations. With growing amount of 2C8 surfactant the band was shifted from the position characteristic for disordered *gauche* conformers (5816 cm^{-1}) to lower wavenumbers (5804 cm^{-1}) indicating the increasing number of ordered all-*trans* conformers. The combination bands of NH_2^+ group were observed in the 4900–4700 cm^{-1} region. At low amount of cations, the NH_2^+ band occurred at 4820 cm^{-1}. With increasing cation content, the shoulder near 4760 cm^{-1} appeared and at 1.0 mmol·g^{-1} concentration this band became dominant while the signal near 4820 cm^{-1} was merely a shoulder. The hydration properties of the samples were investigated by gravimetry and NIR-UpDRIFT technique enabling the measurements of the samples directly in closed glass vials. Difference in the area of the H_2O combination band near 5250 cm^{-1} at 100 % and 0 % of the relative humidity reflected the quantity of adsorbed water. The spectra showed decreasing content of water with growing amount of surfactant. The NIR results correlated very well with the values obtained from gravimetric analysis. The shift of $2\nu_{CH2}$ to the lower wavenumber upon hydration indicated the increasing number of ordered all-*trans* and decreasing of disordered *gauche* conformers. The water molecules evoked the modification of cations configuration from the high degree of disorder to the more ordered. The arrangement of 2C8 cations in Mt interlayers was analysed also during dehydration. Dried and hydrated samples were measured by special NIR-DRIFT temperate cell allowing the in-situ measurement of the spectra in a temperature range 25–125°C. For hydrated 2C8-JP sample the shift of $2\nu_{CH2}$ band to higher wavenumber indicated decreasing amount of *trans* and increasing *gauche* conformer with increasing temperature. Significant shift of this band to higher wavenumber was observed mainly for sample with the lowest cation content (12 cm^{-1}) while no marked shift was observed for sample with higher 2C8 content. Completely different behaviour was noticed in dried 2C8-JP sample where no changes of $2\nu_{CH2}$ position were observed during dehydration even at the lowest 2C8 cation concentration. During dehydration process the changes in the region of combination bands of NH_2^+ group were also detected. With increasing temperature the intensity of the band at 4820 cm^{-1} increased while that at 4760 cm^{-1} decreased. The changes in this region point to the diversity of N-H groups bonding in the 2C8-Mt-H_2O system.

Acknowledgments

The authors acknowledge the financial support of the Slovak Grant Agency VEGA (grant 2/0141/17) and the Slovak Research and Development Agency (grants APVV-15-0741 and APVV-15-0347).

Cation exchange capacity of bentonite in highly saline environment

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Cation exchange capacity (CEC) is one of the basic characteristics of the clays and clay minerals. The value of CEC can be influenced by the nature of the exchangeable and index cations, by the pH value, and by the solution ionic strength (DELAVERNHE et al., 2015). Accessory minerals such as carbonates, e.g. calcite and dolomite, can influence CEC measurement because of dissolution (DOHRMANN, 2006).

In the present study, the CEC of Ca- bentonite Calcigel was studied by Cu-Trien method (MEIER & KAHR, 1999) in the presence of the NaCl in various concentrations (0–20 wt%). These conditions simulate the states of bentonite in geotechnical barriers during hydration by highly saline solutions e.g. in underground radioactive waste deposits.

First, the impact of Cu-Trien (3.33 mmol/L) and NaCl on the carbonate and dolomite solubility were analyzed. Second, the influence of NaCl on the UV/VIS spectra of Cu-Trien was tested. Third, changes in pH value induced by Cu-Trien and NaCl were investigated and finally the CEC of Calcigel/NaCl mixtures were measured and analysed. For comparison, the CEC of Na-exchanged montmorillonite under the same conditions was determined.

Three main factors influencing the CEC determination of Ca-bentonite Calcigel have been identified: I. The changes in carbonates solubility, depending on the variations of NaCl concentrations, as well as on the Cu-Trien aditions. The carbonates solubility increased about 20 % with the addition of Cu-Trien. With the increasing of the NaCl concentration, solubility of the carbonates slightly increased as well. The effect of NaCl was less distinct in the presence of Cu-Trien. II. The spectral behaviour of Cu-Trien changed in the presence of Ca^{2+} and Mg^{2+} cations. The maximum of absorbance was slightly increased and shifted to the higher wavelength in dependence of the concentration and type of cation. III. The pH values have been decreased by the increasing of concentration of the NaCl because of changes of the activity of cations in solution. Decreasing of the pH affects the variable charge of clay minerals that can affect the measured values of CEC.

The impurities of clays, in the form of salts and accessory minerals such as carbonates, significantly affect CEC determination. It is essential to take these effects into account.

Acknowledgments

This study was financed by German Federal Ministry of Economic Affairs and Energy under contract 02E11587A.

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Clay minerals in Icelandic soils - a study on the weathering of tephra and how they impact soil development in South East Iceland

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Iceland offers a rare opportunity to investigate the impact of explosive volcanic eruptions on soil formation, soil weathering processes and soil quality. The volcanically active Vatnajökull area has received numerous tephra deposits of varying thicknesses during Holocene (ÓLADÓTTIR et al., 2011). The presence of the light coloured rhyolitic tephra from the Öræfajökull eruption in AD 1362 and a black coloured basaltic Veiðivötn tephra from AD 1477 in the research area in South East Iceland enable comparison between the weathering behaviour of tephra of different chemical composition and to examine their contrasting mineralogy in both, histosols (wetland soils) and andosols (dryland soils).

Icelandic soils are unique. They are characterized by repeated input of tephra and a steady flux of aeolian material. Even highly organic soils show an appreciable amount of mineral material (leading to andic properties). Weathering rates in Iceland are usually considerable in spite of the predominantly cold climate. Clay minerals are formed in situ and not by translocation, leaching or precipitation in subsurface horizons (ARNALDS, 2008; DAHLGREN et al., 2004). Amorphous secondary minerals (e.g. allophane and imogolite) and poorly crystalline ferrihydrite are the dominant phases (STEFÁNSSON & GÍSLASON, 2001), while layer silicates are either absent or constitute only minor components of the clay fraction in Icelandic soils (e.g. WADA et al., 1992).

Previous investigations on Icelandic histosols show, that the mineralogy of the rhyolitic tephra from AD 1362 is almost entirely comprised of quartz, suggesting that it has hardly altered since its deposition. In contrast, the basaltic tephra (AD 1477) shows more signs of weathering, even though it is younger and therefore exposed to soil forming processes for a shorter period of time. The weathering behaviour and the alteration products formed in the soils are controlled by the composition and characteristics of the parent glass. A prevailing low pH and the high SOM content inhibited clay formation. The presence of amorphous secondary clay minerals can be explained by aeolian deposition of allophanic material. In the clay fraction of the histosols we identified 2:1 layer silicates (e.g. smectite and hydroxy interlayered minerals).

We will present (1) the weathering behaviour of tephra deposits in histosols and andosols, (2) the role of the chemical composition of the tephra for pedogenesis and (3) the mineral transformation in tephra and Icelandic soils.

Acknowledgements
The present research was supported by The Icelandic Research Fund (no., 1201211021), the Austrian Agency for International Cooperation in Education & Research (Marietta Blau Grant), the Erasmus+ Grant and the Friends of Vatnajökull Fund.

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Artificially induced clay mineral authigenesis in an underground gas storage field, North Alpine Foreland Basin, Austria

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Secondary processes within reservoir sandstones during and after hydrocarbon production are poorly understood. This study focusses on the effect of secondary water fill on a sandstone reservoir within a time span of eight years. The reservoir rocks consist of medium grained litharenites with large clasts of shales and carbonates. They originate from a depleted gas reservoir which has been converted into an underground storage field for natural gas. Gas production caused a rise of the gas-water-contact of about 30 m. Based on their initial and final gas and water saturations, four zones can be identified.

Observed diagenetic changes in all four zones include carbonate cementation, K-feldspar overgrowths, authigenic quartz overgrowths, pyrite formation, and poorly crystallized authigenic clay minerals. However, the authigenic clay mineral fraction differs significantly within the zones. Total clay mineral content and crystallinities of smectite, chlorite, kaolinite and illite increase from the gas-bearing to the initial water zone. Additionally, expandable clay minerals and kaolinite were not identified in the gas-bearing zone. This is different in the secondary watered zones, where smectites and kaolinite are developing. The study shows that within a maximum of eight years from the initial flux of water into the gas zone new clay minerals are forming.

The reduction of porosity and permeability caused by this anthropogenically induced process might continue and can also be of relevance within other producing reservoirs, where water saturation increases during production.

Clay mineralogy of the Kışladağ porphyry Au deposit (Uşak, western Turkey): Evidence for an epithermal overprint

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The Kışladağ Au deposit is the first porphyry type deposit in western Turkey and is related to intrusive and sub-volcanic rocks (i.e., Beydağı volcanic complex; 17.3 to 12.2 Ma) that resulted from an extensional tectonic regime in western Anatolia (KARAOGLU & HELVACI, 2012). The main lithologies of the deposit area are quartz-trachyte to quartz-latite flows and volcanoclastic rocks intruded by a series of nested subvolcanic porphyritic intrusives of alkali affinity (BAKER et al., 2016). This study evaluates the clay mineralogy combined with new age data from geochronology of illites in the alteration zones. Clay minerals were characterized by optical and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) methods. K/Ar dating was undertaken on pure alunite and illite-rich clay samples. In order to avoid magmatic micas and potassic alteration related coarse biotites, 0.5–0.2 μm and <0.2 μm grain sizes were extracted for age determinations.

In the Kişladağ porphyry Au deposit, three different phases of intrusions (IN-1 to 3) have been identified from their cross-cutting relationships, alteration and mineralization (BAKER et al., 2016). IN-1 is the oldest and best mineralized (0.86 g/t Au) intrusive phase and forms the core of the system. Alteration samples from IN-1 are characterized by tourmaline bearing quartz veins and fine-grained (sericitic) biotites. IN-2 is a fine to medium-grained porphyritic rock, and intense pervasive clay-quartz alteration appears to have selectively overprinted IN-2A (0.55 g/t Au). IN-2A samples are characterized by an abundance of fine-grained (sericitic) white K-mica (illite) and completely sericitized feldspar phenocrysts. Intrusion IN-3, the youngest intrusive body (<5 to 200 ppb Au), is a fine grained porphyritic rock and contains unaltered plagioclase, with rare quartz and biotite phenocrysts. The volcanoclastic rocks cover a wide area and show fine grained fragmental ash fall tuffs with pumice fragments and porphyritic flows.

The samples from IN-1 contain quartz and clay minerals (illite and rare kaolinite). Illites were commonly developed as fine grained (<2 μm) flakes, with Kübler index (KI, $\Delta°2\theta$; KÜBLER, 1968) values (mean 0.54 $\Delta°2\theta$) and polytype ($1M + 1M_d$) data indicative of a high-grade diagenetic zone (<200°C). The presence of $1M$ illites is indicative of volcanic-hosted hydrothermal alterations (BOZKAYA et al., 2016). The d_{060} value (1.5012 Å) of illite indicates a dioctahedral composition. The samples from IN-2A contain quartz, adularia and clay minerals (illite, kaolinite, smectite and rare chlorite) with KI data (mean 0.52 $\Delta°2\theta$) showing a similar grade to IN-1. Alunite, jarosite and tourmaline are found both IN-1 and IN-2A, whereas hydrothermal biotites are only found in IN-1 and illites dominate in IN-2A. The volcanoclastic rocks are composed of quartz, alunite and kaolinite indicating argillic alteration. Therefore, although the mineralogy-petrography confirms potassic and sericitic/phyllic alterations in IN-1 and IN-2A, respectively, clay mineralogical associations and the crystal chemistry of illites demonstrate an argillic overprint.

The K/Ar ages of illites from both IN- 1 and IN-2A become younger as the grain size decreases. The 0.5-0.2 μm grain size is between 17-15 Ma, whereas the grain size of <0.2 μm is between 14-13 Ma. The age of alunites from volcanoclastic rocks have been determined as 17.6 ± 0.5 Ma. Younger ages for fine grained illites confirm the argillic alteration overprints after potassic and sericitic/phyllic alterations.

The data indicates an epithermal overprint shortly after the potassic and sericitic/phyllic alteration of the porphyry system and shows the duration of hydrothermal activity and mineralization was at least 5Ma.

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Illitization age data on pre-Alpine geological events: an example from the autochthonous Paleozoic sequence, Tauride Belt, Southern Turkey

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The Paleozoic units of the Perigondwanan Eastern Tauride Autochthon representing the eastern extension of the Autochthonous Geyik Dağı Unit exhibit regular and almost continuous outcrops between Sarız (Kayseri) and Tufanbeyli (Adana). Sudden changes in diagenesis/metamorphism of Paleozoic sedimentary sequences together with the increasing depth may indicate stratigraphic irregularities or possible tectonic events. This study aims to re-evaluate the geodynamic models of the northern Gondwana-margin through geochronology of illite diagenesis in the Late Silurian to Late Devonian shales exposed between Sarız and Tufanbeyli. In this context, K/Ar and Rb/Sr isotopic age dating was carried out on pure diagenetic illite samples which were also investigated by textural-mineralogical (BOZKAYA et al., 2002; BOZKAYA & YALÇIN, 2004) and organic petrographic (vitrinite, vitrinite like solid bitumen and bitumen reflectance) methods. In order to eliminate detritic illite/micas, fine grain sizes (2.0–1.0 µm, 1.0–0.5 µm, 0.5–0.2 µm and <0.2 µm) were extracted and illite polytype ratios [$2M_1$ / ($1M$ + $1M_d$)] were calculated for each grain sizes.

The illitization (diagenesis) ages for diagenetic illites ($1M$+$1M_d$) range from 264 Ma to 315 Ma, which corresponds to the unconformity between the Carboniferous and Permian that was previously reported for the Tauride units (ÖZGÜL, 1976). The fossil findings from the youngest strata below the unconformity plane indicate the Early Carboniferous (Early-Middle Mississippian) whereas the oldest rocks above it are of late Middle Permian-Late Permian age, indicating a gap of >70 Ma. Illite Kübler index data (KI, Δ°2θ) indicate lower parts of high-grade diagenesis (0.82-0.85 Δ°2θ) for Silurian-Carboniferous, whereas low-grade diagenesis (>1.00 Δ°2θ) for Permian-Triassic units. Organic matter (vitrinite, bitumen) reflectance (OMR) data for Permian (R_{max}=1.33 %) and Carboniferous (R_{max}=1.83 %) units correspond to paleotemperatures of ~120ºC and ~170±30ºC assuming normal heat flow ~60 mW/m^2 using the KI-T°C-OMR correlations of FERREIRO MÄHLMANN et al. (2012) and FERREIRO MÄHLMANN & LE BAYON (2016). This data indicates the discordance, i.e., a diagenetic/metamorphic jump reflecting a sedimentary hiatus, which appears to be associated with thermal event. This thermal event coincides with the maximum burial depth obtained from the Paleozoic subsidence curve of the Geyik Dağı Unit (GÖNCÜOGLU et al., 2004).

The mineralogic and organic petrography-based evaluations from the Perigondwanan Tauride Autochthon, confirmed by radiometric age data, indicate a Variscan regional geological event, which may have potential for re-evaluation of geodynamic models of the northern Gondwana-margin during the Late Paleozoic. The KI-OMR comparison testifies different thermal gradients below and above the hiatus.

Acknowledgments
This study is partly supported by the Turkish Research Fund (TUBITAK Project No 115Y420).

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Hydro-mechanical behaviour of the MX-80 bentonite and bentonite-sand mixture hydrated with brine

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The Canadian Nuclear Safety Commission (CNSC), Canada's nuclear regulator, conducts regulatory research in order to build independent knowledge on safety aspects related to the deep geological disposal of radioactive wastes. In addition to the geological barrier, a major safety component of the repository system consists of engineered buffer and seal materials such as MX-80 bentonite containing highly expansive clay minerals that will swell when they interact with pore water. Site characterization at a candidate site in sedimentary rock in Southern Ontario, Canada shows very high salinity (200–350 g/L) in pore water at about 400 m below the ground surface. Experimental evidence shows that salinity plays an important role on the hydro-mechanical behaviour of a bentonite buffer and seals. However, the experiments conducted so far have mostly been performed at salinity concentrations much lower than the 200–350 g/L concentration levels of Canadian brines. For a deep geological repository (DGR) proposed in Canadian sedimentary rocks, there is a strong need to understand the interaction between brine and bentonite-based buffer and seal materials, in order to assess their long-term performance as a barrier to contaminant transport.

In this study, laboratory experiments were performed to investigate hydro-mechanical behaviour, including swell pressure, compressibility, and permeability of MX-80 bentonite and bentonite-sand (70-30) mixture using brine model water (MW) and deionized water (DI) as pore water. The MW is based on thermodynamic modeling, and its element concentrations match the mean measured concentrations from the proposed DGR site for Cl, Na, K, Br, with small deviations for Ca and Mg. The experimental results show that the swell pressure of the MX-80 bentonite and the bentonite-sand (70-30) mixture measured under zero-volume-change and one-dimensional (bottom-up) hydration conditions is substantially decreased by high pore water salinity. Interactions between the MW and the bentonite decreased the swell pressure of MX-80 by a factor of 8 relative to DI water, from a peak of 2800 kPa with DI water to 350 kPa after 1 year with the MW at a reference dry density of 1.6 Mg/m^3. Initial swell pressures with the MW were 2.6 times larger at a higher dry density of 1.68 Mg/m^3, but still reduced to 750 kPa after 1 year of MW hydration. MX-80 bentonite and the bentonite-sand mixture are less compressible when hydrated with the brine model water. The swelling index of the bentonite and the bentonite-sand mixture hydrated with the MW is much smaller than that of the same materials hydrated with the DI. Despite interactions between the MW and the MX-80 bentonite that increase the permeability by two orders of magnitude, very low hydraulic conductivity of 4.4×10^{-11} m/s on average was measured after one year of permeation by the MW at a dry density of 1.6 Mg/m^3. However, MX-80 bentonite-sand mixtures tested at a dry density of 1.63 to 1.67 Mg/m^3 were unable to attain very low hydraulic conductivity, with values tending to 4×10^{-9} m/s after one year of permeation with the MW, which are three orders of magnitude higher than for permeation with the DI.

Acknowledgments
This study was financed by the Canadian Nuclear Safety Commission under the contract no. 87055-14-0228. All experiments were performed by the GeoEngineering Center, at the Department of Civil Engineering, Queen's University.

Application of silver- bentonite in nuclear waste treatment

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The correct handling of radioactive waste and its isolation from the environment is a particularly important task. This is important not only for the protection of the population but also for the protection of the living space of natural organisms (NAGY & KÓNYA, 2009). With this work we can contribute to the development of the best practices, in which radioactive waste can be stored in a safeway. The purpose of the work is to produce the modified clay, the cation of which precipitates with the anionic impurity and thereby binds it. In their natural state, raw bentonites preferably adsorb cations due to negative layer charge. However, some of the radionuclides (e.g. ^{131}I and ^{36}Cl) are present as anions. Thus modified bentonites are needed for the sorption of these radionuclides. In this study, Ca-bentonite is used because it is ubiquitous in nature, easily accessible and its main mineral, the montmorillonite, binds cations in its interlayer space, which can be modified to the desired quality, so finding a solution for sorption of radioactive anions would be economical and useful.

In this work, the interaction of ^{131}I and ^{36}Cl ions were studied with silver ion modified bentonite because the resulting silver iodide is a hardly soluble precipitate which makes the clay suitable to bind the halogenide ions. The kinetics, equilibrium time, sorption isotherms and the d(001) basal spacing of Ag-montmorillonite were determined.

The first step was to modify the Ca-bentonite with silver ions. The Ag concentration of silver-bentonite was measured by X-ray fluorescence analysis, 75 % of the cation exchange capacity (CEC) was exchanged by silver ions in one ion exchange. After that sorption experiments with iodide and chloride ions were carried out by batch technique.

The sorption is fast, the equilibrium is reached within some minutes. The Langmuir equation was used to determine the number of active sites and the solubility of bentonite-silver -iodide and bentonite-silver -chloride ion complexes. Since the number of active sites decreases as the temperature increases in the case of chloride sorption, the exothermic reaction is supposed. In contrast, iodide sorption is an endothermic reaction. A decrease in d(001) basal spacing of montmorillonite was observed after ion exchange and after iodide sorption too. Potassium ions decrease the sorption of iodide as a result of the supposed montmorillonite-illite transformation.

In this study, silver- bentonite was successfully tested for removing halogenide ions.

Acknowledgments

This study was financed by by the EU and co-financed by the European Regional Development Fund under the project GINOP-2.3.2-15-2016-00008.

The work was supported by the Hungarian National Research, Development, and Innovation Office (NKFIH K 120265).

The authors thank Peter Konya for the X-ray diffraction measurements.

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Healing clays from Santa Maria (Azores, Portugal): assessment of their potentialities

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Azores volcanic islands have, in general, very good potentialities in what concerns healing geomaterials (residual clays and/or volcanic muds). Previous studies showed that São Miguel volcanic muds present very high quality, regarding mineralogical, geochemical and physical (thermal and rheological) characteristics, to be used for pelotherapy. However, their occurrences are of small dimension, demanding a blending process with similar geomaterials occurring nearby in higher quantity. Residual clays are very abundant on Santa Maria (another Azores island next to São Miguel) which have been exploited in the past as ceramic raw materials. Thus, a sampling campaign was performed on Santa Maria, focused on the most weathered formations; a total of sixteen samples were collected. Several properties such as: textural analysis (by wet sieving and Sedigraph grain size analysis), mineralogical composition (qualitative and semiquantitative, by XRD), chemical analysis (major and trace elements, by XRF), crystallochemistry composition (SEM/EDS), cation exchange capacity (CEC), exchangeable cations, abrasiveness, Atterberg Limits and Plasticity Index, Specific Surface Area, thermal properties (ATD, DTG, Specific Heat and cooling rate), and pH were determined, in order to assess if the materials have suitable properties for healing proposes. All tests were performed on fraction inferior to 63 micrometres, with exception of SEM, done on clay fraction (under 2 micrometres). All these analyses and tests were performed in accordance with the protocols and norms followed in the Departments of Geosciences and of Materials Engineering of the University of Aveiro. All samples are very rich on phyllosilicates and Fe oxides/hydroxides. Kaolinite is the main clay mineral of all samples. Chemical composition is dominated by Al, Si and Fe oxides. CIA (Chemical Index Alteration) was also determined, revealing a high alteration stage all around the island. The obtained properties are, in a general way, favourable, revealing the potentiality of Santa Maria residual clays to be blended with São Miguel volcanic muds.

Acknowledgments
Supported by GeoBioTec Research Centre (UID/GEO/04035/2013), funded by "Fundação para a Ciência e Tecnologia" (FCT, Portugal), FEDER funds through the Operational Program Competitiveness Factors COMPETE. FCT granted the second author a PhD scholarship (SFRH/BD/102837/2014).

Geochemistry of volcanic clayey soils from Santa Maria (Azores, Portugal)

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A research project is underway to characterize the properties of volcanic muds and residual and sedimentary clays from the mid-Atlantic Azores archipelago (Portugal). Santa Maria Island deserves special attention not only because it is the only one (of Azores) where sedimentary formations do occur but also due to the intense surficial alteration presented by some of the volcanic formations. This intense alteration gave place to the formation of several clay quarries, once exploited for ceramics but nowadays abandoned. The main goal of the present work is to assess the degree of alteration and its influence on the development (qualitative and quantitative) of residual clays deposits. For this specific work, twenty samples from Santa Maria Island were collected on May, 2017, and fully characterized in terms of mineralogy, geochemistry and crystallochemistry. Geochemical composition was assessed (on fine fractions) by X-ray fluorescence spectroscopy (XRF) using an Axios PANalytical spectrometer equipped with Rh tube, argon/methane gas and IQ + (major elements) and Pro-Trace (minor elements) data processing programs. Mineralogical studies were carried out on random-powders (fine fractions) and oriented aggregates (clay fractions) through X-ray diffraction (XRD) on X'Pert PW 3040/60 equipment using Cu Kα radiation. Crystallochemistry was studied by Scanning Electron Microscopy (SEM-EDS), on clay fractions, using a Hitachi S4100; structural order of the main clay mineral (kaolinite) was assessed through the Hinckley Crystallinity Index. Weathering indices were calculated, from fine fraction geochemical data, namely CIA (Chemical Index Alteration), MIA (Mafic Index Alteration), WIP (Weathering Index of Parker), CIW (Chemical Index of Weathering) and R (Ruxton Ratio). Studied samples are all very fine-grained and very rich in phyllosilicates and Fe oxides/hydroxides. Kaolinite is the main clay mineral of all samples. Chemical composition is dominated by Al, Si and Fe oxides. The alteration results revealed that all samples are highly altered, with values rounding to 80 % and 99 % for CIA and CIW, 78 % and 99 % for MIA, 340 and 4300 for WIP and 1.2 to 3.4 for R.

Acknowledgments

Supported by GeoBioTec Research Centre (UID/GEO/04035/2013), funded by "Fundação para a Ciência e Tecnologia" (FCT, Portugal), FEDER funds through the Operational Program Competitiveness Factors COMPETE. FCT granted the second author a PhD scholarship (SFRH/BD/102837/2014).

Comparison of swelling behaviour and hydraulic conductivity of clay pellets for sealing purposes in the framework of geotechnical applications

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Due to a low hydraulic conductivity after swelling combined with environmental sustainability, clay composites offer a broad spectrum of application in environmental geotechnics. Fabricated as extruded clay pellets and poured into cavities, they are used as sealing of well constructions or backfilling of drill holes and mining shafts. The bulk density and the initial water content of the pellets for these applications ranges from about 1.07 to 1.27 g/cm3 and from 10 to 25 %, respectively. Besides initial density (SCHANZ & TRIPATHY, 2009) and water content, the mineral composition of the clays, the geometry of the pellets, and the technology applied for producing the pellets is substantially affecting the sealing performance of the pellets in these applications.

For a proper handling of the material in its particular practical application, it is necessary to be aware of the characteristic hydro-mechanical behaviour of the used clay pellets. For some products an initial contact with water results in considerable settlement (collapse), while for other products this observation cannot be proved. Besides the maximum and equilibrium value of the swelling pressure, also its development (e.g. rate) varies significantly. Furthermore, the consistency and therefore strength of the swollen and fully saturated materials range from liquid to solid state.

The objective of this study is to classify various tested clay pellets with respect to their swelling behaviour, sealing capability and final consistency. Hence, swelling pressure tests are conducted followed by hydraulic conductivity tests in constant volume cells with defined and consistent boundary conditions for different products available at the European market (anonymised). Prior to testing, the clay pellets were ground to a diameter of 2–4 mm and the initial bulk density of the specimens corresponded to the known bulk density of the pellets. The used cells were designed, constructed and calibrated at the Chair of Foundation Engineering, Soil and Rock Mechanics at Ruhr-Universität Bochum (KHAN, 2012; BAILLE et al., 2010). After dismantling the tests, the final water content and density were determined in three layers of the specimen and thus, the final degree of saturation was calculated. Further, the structure stability was measured with a pocket penetrometer.

The obtained swelling pressures and permeability values for the different varieties of clay pellets were compared and their behaviour was interpreted with respect to the mineralogical properties of the clays.

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Rheological properties of bentonite and palygorskite suspensions after dynamic aging at high temperatures

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Recent advances in the drilling industry have led to the design of the drilling wells at greater depths and demanding environments. In this sense, the exposure of drilling fluids to high temperatures and pressures requires a better understanding of their rheological parameters. Clays and especially bentonites and palygorskite, are commonly used in the formulation of drilling fluids because they form stable and viscous suspensions. However, the rheological properties of the drilling fluids are affected by temperature, with the bentonite fluids being affected also by the presence of electrolytes. In contrast the palygorskite fluids are not sensitive to electrolytes. This study examines the influence of temperature on the rheological behavior of bentonite and palygorskite samples. For this purpose, 4 Wyoming bentonites, one bentonite from Milos Island, Greece, a bentonite rich in nontronite and a palygorskite, both from the Grevena area, Greece were utilized. The quantitative bulk mineralogy of the samples was determined by X-Ray Diffraction (XRD) on random mounts using the Rietveld approach (BGMN code Autoquan® software). The layer charge of the smectites was determined according to (CHRISTIDIS & EBERL, 2003). Li-saturation followed by heating at 300°C for 24 h was used to estimate the beidellitic content of the smectites (Green-Kelly test). DTG-TG analysis was used to determine the dehydroxylation temperature of the smectites. The chemical composition of the samples was determined by X-Ray Fluorescence spectroscopy (XRF). The dynamic aging method was applied (AMERICAN PETROLEUM INSTITUTE 13A, 2010). Hence, 5 % suspensions were prepared and heated at 25 – 176°C under continuous rolling for 16 h. After cooling at room temperature, the rheological properties of the suspensions (apparent viscosity, plastic viscosity and yield point) were determined with a Grace-M3500 viscometer. The filtrate properties of the suspensions after dynamic aging were determined with an API standard filter press at room temperature. The rheograms obtained after aging at the different temperatures were modelled with a MATLAB code, designed to determine rheological behaviors varying among Bingham Plastic, Power Law and Herschel-Bulkley rheological models.

The Wyoming bentonites contain 68-79 % montmorillonite with up to 7 % beidellitic layers, the Miloan bentonite contains 82 % montmorillonite with up to 15 % beidellite layers the nontronite-bearing bentonite contains 65 % smectite and the palygorskite-rich sample contains 83 % palygorskite. All bentonites are dominated by smectites with layer charge of 0.41±0.02 e/huc, i.e. by low charge smectites. The nontronite has layer charge 0.39 e/huc, thus being an intermediate charge smectite. Also, the thermal properties of the Wyoming and the Miloan bentonites are comparable and the main dehydroxylation event is focused at 620-680°C (*cis*-vacant smectites). Nontronite dehydroxylated at 530°C (*trans*-vacant smectite). Therefore the temperatures encountered in the drilling well will not cause dehydroxylation of smectites. Temperature significantly affected the rheological and filtrate properties of the bentonite suspensions. At 25°C three of the Wyoming bentonites and the nontronite displayed Bingham Plastic behavior whereas the palygorskite, the Miloan bentonite and one Wyoming bentonite displayed Power Law behavior. With increasing temperature, the rheological model changed; nearly all suspensions displayed a pseudoplastic behavior and were fitted to Herschel Bulkley or Power Law models. The apparent and plastic viscosity varied between broad limits and gradually increased with increasing temperature up to 149°C. At higher temperatures two of the Wyoming bentonites the Miloan bentonite and the nontronite displayed lower viscosity, whereas in the remaining Wyoming bentonites viscosity continued to increase. In addition, the yield point and the filtrate loss also varied between broad limits and increased with increasing temperature.

The observed differences between the montmorillonite bearing bentonites are not explained by differences in smectite crystal chemical properties, because all smectites have a comparable layer charge and a low tetrahedral charge. The differences in the rheological properties is attributed to the variable degree of hydration of the smectite forming quasicrystals of different thickness, which cannot break up to smaller particles even at high rates of shear. The rheological properties might be improved by using suitable additives or by appropriate processing. In contrast the rheological properties of the nontronite might be attributed to the tetrahedral localization of layer charge.

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Significant bias in clay minerals extracted from ancient carbonates?

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The global geographical distribution of clay minerals, their differential dispersal in platform areas and response to changing sea level can be deduced for ancient carbonates by addressing their clay mineral content. The wide variety of clay minerals responds differently to environmental variations and diagenetic conditions, providing valuable tools to unravel past climate conditions and evolution over time (CHAMLEY, 1997; THIRY, 2000). Due to the lithified nature of the deep-time geological archive, laboratory procedures are mandatory to extract clay minerals from their host carbonates. But these procedures may influence the final clay mineral assemblage, both in quality and quantity. It is here demonstrated how the use of different extraction methods can cause a significant bias in paleoenvironmental interpretations.

Apart from the conventional hydrochloric acid treatment (here at 0.1N at room temperature), a variety of alternative experimental conditions (pH, temperature, reaction time) were tested and compared for carbonate rocks representing different Jurassic and Cretaceous depositional settings, ranging from very proximal shallow-platform areas to more open-marine environments. Alternative extraction protocols include: a one hour treatment with 1N acetic acid at room temperature and at higher temperature (50ºC); increasing acetic acid concentration (2N) and extending reaction-time up to two hours. Mineralogical composition was controlled before and after each test, and was performed on both bulk and clay mineral fractions. This allows a direct evaluation of the treatment effects.

For all tested samples, hydrochloric acid attack provided the least desired outcome, showing a strong depletion in smectite, illite and interstratified illite-smectite on diffractograms. In fact, the presence of these minerals becomes only discrete in these samples, with imperceptible signals along the diffractograms. In clear contrast, acetic acid experimental conditions resulted in a better detection and higher abundance of these minerals, with two to three-time higher peak intensities for smectite and illite. The best results were obtained with 2N acetic acid reacting for 2 hours, showing no major advantages when temperature was increased. This approach is significantly less time-consuming, as well as "clay-friendly". The presence of clay minerals among all tested samples is unequivocal and their relative proportions can easily be determined, allowing the establishment of accurate paleoenvironmental interpretations.

For exactly the same materials, conflicting interpretation of paleoenvironmental scenarios are presented based on results obtained from different experimental approaches on clay mineral extractions from carbonate rocks. This research highlights the importance of favoring less aggressive protocols, showing that acetic acid extraction is much faster and considerably more conservative.

Acknowledgments
R. Coimbra is supported by the Post-Doctoral Fellowship SFRH/BPD/92376/2013 (FCT, Portugal) and the research units GeoBiotec - UID/GEO/04035/2013 and MARE- UID/MAR/04292/2013. Projects HE4467/6-1 (Deutsche Forschungsgemeinschaft -DFG, Germany), CGL2012-39835 (MINECO, Spain) and the Research Group RNM-178 (Junta de Andalucía, Spain) are also acknowledged.

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Sediments lagoons characterization to be used as a therapeutic muds in thalassotherapy

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Sedimentary silty clay sediments (muds) occur in several points of the Portuguese coast, namely in coastal lagoon systems. These sludges are usually rich in clay minerals and organic matter, and have been used, traditionally, by local populations as raw material for a variety of purposes: for the correction of the often salty sandy character of coastal agricultural soils, or to the preparation of peloides (therapeutic sludge) for use in thermal spa. In Portugal, peloids obtained from sludge collected from the Pateira de Fermentelos lagoons near Aveiro were used and duly cleaned and prepared for later maturation in tanks fed with sulfur water at 37–39ºC for 6 months, in order to acquire a very high amount of sulfur, a practice used for years in the Spa of Vizela and the Spa of Aregos. Some muds were then used in the therapy of rheumatic diseases and other musculoskeletal diseases or in the treatment of eczematous dermatoses (namely psoriasis).

The mineralogical composition of "muddy" sediments, particularly its fine and clayey fractions, shows a predominance of silicate detrital minerals (such as quartz, feldspars and phyllosilicates); the most common minerals are also present, such as accessories, opal C/CT, gypsum, anhydrite, zeolites (mainly clinoptilolite-heulandite), pyrite, siderite, calcite and dolomite. The chemical composition is mainly aluminosilicate, with average contents (%) in Al_2O_3 of 21.55 and in SiO_2 of 51.24. Potentially toxic elements (PTE) do not present values above those of reference.

These muddy sediments have an appropriate mineralogical and geochemical composition with values above the minimum requirements for clay minerals and trace elements desired and, on the other hand, below the dangerous levels for heavy metals.

The studied samples show adequate values for their use in topical dermocosmetic applications, namely low abrasiveness and cooling kinetics, and high plasticity, exchangeability, absorption and specific heat. On the other hand, they present very interesting values for the trace elements, namely in the form of exchange cations, and do not present values above those tolerated for the potential harmful elements (PHE).

Acknowledgments

This research was financially supported by Fundação para a Ciência e Tecnologia (FCT) grant SFRH/BD/102837/2014 and Project UID/GEO/04035/2013

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Adobe formulations for rehabilitation of old buildings (in Portugal)

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Adobe is an extremely simple form of earth construction and with this technique the shrinkage associated with the construction of large structures is avoided. In Portugal, earthen materials have been used in load-bearing walls in the form of adobe or rammed earth for the construction of buildings especially in the southern and central coast. Portugal has favourable weather conditions for earth construction. However, with the evolution of building materials, this construction technique was almost abandoned. Nevertheless, recently there has been an increased interest on earth construction in order to preserve the cultural heritage focused in the rehabilitation and conservation of this type of buildings. Adobe has been used in several types of construction: rural and urban buildings, many of which are still in use; walls to outline the boundary of properties; water wells; churches; warehouses. The use of adobe construction in the Aveiro district reflected the properties of the existing raw materials available, namely sand, clay sediments and soils and lime (SILVEIRA et al., 2012), and there is an evident heterogeneity of the adobes linked to the geographic distribution of the available resources. In Aveiro area there was a semi-industrial production of adobe, with some small companies employing 'adobeiros', for the manufacture of blocks of adobe, along with a domestic self-production (COSTA et al., 2016).

Most conventional consolidation treatments used in the past have not succeeded in providing a long-term solution to rehabilitation of the adobe buildings, because they did not tackle the main cause of degradation, the expansion and contraction of constituent clay minerals in response to humidity changes. Clay swelling could be reduced significantly by transforming clay minerals into non-expandable binding materials with cementing capacity using alkaline activation. Take this into account, the purpose of this study was to develop adobes with water, NaOH, KOH, and $Ca(OH)_2$. The adobes tested with water were used as reference (blank). Mineralogical composition (XRD), chemical composition (XRF), mechanical strength, water absorption capacity, chemical resistance, particle size, and specific surface area were determined for these four formulations. The obtained results allowed concluding that the adobes with NaOH and KOH had improved properties. On the other hand, the activation with $Ca(OH)_2$ did not improve the properties for the adobe blocks formulations. In terms of future work these materials will be tested on industrial scale to better evaluate their potential applications from both technological and economical points of view.

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Influence of the synthesis precursors of layered double hydroxides on the removal of chromium species from aqueous solutions

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Layered double hydroxides (LDH), usually called hydrotalcites, are classified as anionic clays, with general formula of $[M(II)_{1-x}\ M(III)_x\ (OH)_2]\ (A^{m-})_{x/m}.\ nH_2O]$, where M(II) is a divalent cation, M(III) is a trivalent cation, A is an anion with charge m^-, and x is the M(III)/(M(III) + M(II)) molar ratio. Hydrotalcites or the mixed oxides obtained after calcination present interesting properties and many applications since they present large specific surfaces, basic character, high metallic dispersion and high thermal stability. Several authors have studied the influence of the synthesis variables such as pH and calcination temperature among different metals on the structural properties of the hydrotalcites and, also, the adsorption variables in nanoparticles with different pollutants (ZUBAIRA et al., 2017).

In this work, a series of MgAl hydrotalcites and the oxide mixture obtained by their calcination at 500°C were synthesised by coprecipitation from metal nitrates and by using two different coprecipitation salts, Na_2CO_3 and K_2CO_3, named MgAl-Na and MgAl-K, respectively. The third solid used was a commercial MgAl hydrotalcite (MgAl-N), synthesized only in presence of NO_3^- ions. The effect of the different coprecipitation agents used during the preparation on the functionality of the clay as adsorbent of contaminated aqueous effluents, as chromium species, was investigated. The solids were characterised by studying their textural properties by adsorption-desorption isotherms (S_{BET}-N_2), their thermal behaviour by thermogravimetric analysis (TGA-DTA), their crystal structure by X-ray diffraction (XRD), and the presence of anions in the interlayer space was determined by Fourier transform infrared spectroscopy (FTIR). The capacity for the removal of $Cr_2O_7^{2-}$ ions was evaluated by preparing suspensions with 70 mg of each oxide sample (MgAl-Na, MgAl-K and MgAl-N), in 20 mL of a potassium dichromate solution (Mallinckrodt) with a concentration of 800 ppm.

From the results, it can be observed that the three solids reached the higher retention of the aqueous pollutant at different times. The MgAl-K solid presented the lowest removal, being almost negligible in comparison with the others. At 24 hours, MgAl-Na retained 87 % of the chromium species, reaching the maximun saturation, while only after 72 hours of contact; the MgAl-N retained 90 % of the pollutant. A longer contact time does not cause an increase in contaminant retention, as has already been reported in the literature (DAS et al., 2004). From the XRD analysis it can be inferred that the removal of the dichromate ions from the aqueous medium would allow the reconstruction of the structure and the ions would be placed in the laminar space, since this type of clay has the memory effect property. The diffractograms of the hydrotalcites synthesized with carbonate ions in the interlaminar space and the hydrotalcites obtained when the oxides obtained after the calcination were in contact in solution with the dichromate ions, for 24 hours were compared. The solids, which have crystalline structure, exhibit a slight shift at lower diffraction angles, which indicates the presence of the chromium species in the interlaminar space, due to a greater interplanar distance compared to those with intercalated carbonate ions.

As a conclusion, the nature of the coprecipitation agents does not affect the formation of the laminar structure and the only crystalline phase that can be observed after calcination is the oxide of the divalent cation. On the contrary, it was observed that the carbonate salt has a strong impact on the dichromate ions removal, the sodium one with being the most effective solid to remove these ions.

Acknowledgments
This study was financed by CONICET, UNSL and ANPCYT. The authors would like to thank Dra. Mosconi for the FTIR analysis, Lic. Fixman for the textural properties analysis and Dr. González for the XDR analysis.

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Clay minerals in the Upper Permian evaporite deposits from the Mali Kukor, Vranjkovići, and Slane Stine (Dalmatia, Croatia)

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The studied evaporite deposits (Mali Kukor, Vranjkovići, and Slane Stine) are located in the central part of middle Dalmatia, Croatia. In this region, Upper Permian evaporite sediments were deposited under favourable conditions onto the Variscan basement around the northern margins of Gondwana. The characteristics of these sediments are indicative of deposition in supratidal and sabkha settings (i.e., early diagenetic dolomites and evaporites) within a shallow epicontinental marine environment with highly varied coastlines, bays, and lagoons (DEDIĆ et al., 2018).

Mineralogical composition of Upper Permian evaporite sediments in central part of middle Dalmatia was investigated to determine the type and extent of outcrop weathering alteration and to explore the preservation of diagenetic clays in changing geochemical environments. The clay minerals of Upper Permian evaporite sediments have been studied by X-ray diffraction (XRD) on 21 oriented samples. The evaporite sediments were collected from the outcrops in deposits, while clastic sediments from the surrounding area (Mali Kukor, Garjak and Suhač). The deposit of Mali Kukor is dominated by gypsum, anhydrite and calcite, Slane Stine by gypsum, anhydrite and dolomite, while Vranjkovići by gypsum and dolomite. The clay mineral association of insoluble residue of evaporite sediments in these deposits mainly consists of illite, illite-smectite, smectite, chlorite and kaolinite. Clay minerals in Mali Kukor vary from illite, illite-smectite and smectite in upper evaporite units to illite, chlorite and kaolinite in lower units. In Slane Stine evaporite deposits, the clay minerals are represented by illite, chlorite and kaolinite, while in Vranjkovići deposits the dominant mineral in the clay fraction is illite, with occasionally appearances of chlorite and kaolinite. Clay minerals in clastic sediments are represented by chlorite, illite and kaolinite, while in one locality vermiculite and illite are present.

A variety of clay minerals are commonly found in shallow epicontinental marine environment and clay minerals also form a considerable portion of the sedimentary successions accumulated under evaporitic conditions in continental settings of the past. The clay minerals are products of weathering of rocks or precipitation reactions in saline solutions where surface conditions favour hydrous minerals (MEUNIER, 2005). The type of the clay minerals forming from rock weathering is a function of precursor rock type, chemistry of interacting fluids, and intensity of weathering i.e., humid vs. arid climates; where moderate weathering produces smectite and intense weathering produces kaolinite (MEUNIER, 2005). The produced clay minerals behave as detrital minerals so they can be carried to sedimentary basins via erosional processes. Mechanisms of clay formation include: transformation from detrital precursors via solid-state substitutions or micro-scale dissolution/precipitation reactions, topotactic growth onto precursor minerals, and direct precipitation from solution or neoformation (HAY & KYSER, 2001; DEOCAMPO et al., 2009; BRISTOW & MILLIKEN, 2011). It is concluded that the clay minerals in Upper Permian evaporite sediments are detrital in origin, they reflect the character of their source material, and are slightly modified in their depositional environments. The illite, chlorite and kaolinite assemblage is typical for clastic sedimentary environments with a medium to high dynamics, while smectite indicates high hydrodynamics (CHAMLEY, 1989). Diagenesis and transformation can be determined in Vranjkovići deposits where illite is the dominant clay mineral, while upper units in Mali Kukor deposit is predominated by smectite and mixed-layer illite-smectite which point to different depositional conditions.

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Synthesis and multi-analytical characterization of hydroxy-interlayered smectite (HIS)

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Chemical and physical soil properties are determined crucially by both the clay mineral content and the chemical and mineralogical composition of the clay-sized fraction. The clay mineralogy of soils is known to be a complex issue and especially the acidic weathering of soils leads to a high diversity of discrete and interstratified clay minerals. Especially during the acidic weathering of soils primary silicates such as feldspars or chlorites are transformed to intermediate phases, especially clay minerals. During this process aluminium (Al) is dissolved and mobilized as Al^{3+} exchanging interlayer cations of expandable clay minerals such as smectite or vermiculite. Al^{3+} polymerizes in the interlayer region forming oligomers (Hydroxy-Interlayers, HI). These oligomers cause a reduced expandability of smectite and vermiculite, and thus, a reduced soil fertility and water capacity. Although these Hydroxy-Interlayered Smectite (HIS) and Hydroxy-Interlayered Vermiculite (HIV) phases are known for a long time, they are still challenging to characterize and quantify.

The aim of the present study was to create a sample set of highly enriched HIS samples each with a different degree of hydroxy-interlayering spanning the range between 0 % and almost 100 % of HI. These samples are supposed to be used to create a structural model which can be applied to Rietveld analytics to be able to quantify the amount of HIS in artificial and natural samples (e.g., soils).

A sample set of eight HIS samples with different degrees of hydroxy-interlayering ranging from 0–90 % mol/mol was prepared from the Na^+-saturated <2 µm fraction of a natural bentonite sample from Milos, Greece. Different amounts of a 0.1 mol/L $AlCl_3$ solution were added and different reaction times used to create samples with a different degree of hydroxy-interlayering. The products were investigated using a large number of different methods such as X-ray diffraction (XRD), Infrared spectroscopy (IR), X-ray Fluorescence spectrometry (XRF), Fe^{2+}:Fe_{total} determination, Solid State Nuclear Magnetic Resonance spectroscopy (NMR), Simultaneous Thermal Analysis coupled with Mass Spectrometry (STA-MS) and Cation Exchange Capacity (CEC) determination.

NMR spectroscopy showed that newly formed Al, both as interlayer oligomers and precipitated $Al(OH)_3$ phases had exclusively 6-fold coordinated Al whereby the precipitation products showed a slight chemical shift (+3 ppm) and therefore could be distinguished from the HI. With the help of chemical calculations the interlayer oligomers were characterized regarding both their average charge per Al and their average degree of polymerization. Additionally, based on CEC data the degree of hydroxy-interlayering was determined for each HIS sample. The interlayer oligomers were found to be mono- to pentamers whereby the average oligomer size increased and the average charge per Al decreased with increasing degree of hydroxy-intercalation, indicating an *in-situ* polymerization in the interlayer regions. Based on XRD data and the average degree of polymerization (oligomer size), a structural formula of each HIS was calculated. As a cross-check, the theoretical CEC value was calculated from these formulas and compared to measured values. Both values were found to correspond each other ($R^2 = 0.9989$) with only a slight systematic error ($y=0.9787x$).

The calculations presented, although being complex, can be applied to natural systems such as soils to characterize the hydroxy-interlayering if the amount and the crystal chemistry of admixed phases are known. The sample set produced and characterized here will be used in further studies to create a structural model for HIS suitable for Rietveld refinement to quantitatively determine the amounts of HIS in natural and artificial samples.

Effect of disaggregation energy on amounts of clay fractions and the clay mineralogy inventory

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Clay rocks are analyzed for the clay minerals inventory, however, all techniques require disaggregation for suspension of clay-sized particles (<2 µm). Disaggregation is assumed to produce representative clay fractions with respect to mineralogy and total amounts of clay fractions. Comparing lab protocols for clay rocks with those from fields of soil science (ISO, 2002) or geotechnics (ISO, 2017) shows a lack of standardization for “geologic samples”.

The aim of the study is to show the effect of different disaggregation energies applied during sample disaggregation on i) amounts of clay fractions and ii) the clay mineralogy inventory gained using these different techniques: 1) ultrasonic bath, 2) stirrer, 3) end-over-end shaker, 4) 2x20 sec. ultrasound sonotrode, and 5) 2x2 min. ultrasound sonotrode. Results clearly indicate that for Lower Cretaceous rocks from bore holes in Northern Germany total amounts (fraction <2 µm) vary by a factor of 2 while clay minerals inventories vary only slightly.

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Use of Fe/Mn – modified aluminosilicates as selective anionic sorbents

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Aluminosilicates represent a feasible and challenging material due to several aspects, such as its chemical stability, availability, environmental safety issues, fineness, and appropriate surface properties. Most of them belong to low-cost and environmentally acceptable materials. In water systems at pH ≈ 5 and above, aluminosilicates are typical cation-selective sorbents thanks to low pH of zero point of charge (pH_{ZPC}). Recently described method of their surface modification with Fe/Mn ions has expanded their possible use in adsorption processes due to the change of surface charge (pH_{ZPC}) causing a strong selectivity to anions (DOUŠOVÁ et al., 2006). Three pre-treating methods including Fe^{II} (BONNIN, 2000), Fe^{III} (IZUMI et al., 2005, modified), and Mn^{II} (HERZOGOVÁ, 2014) were applied to different types of aluminosilicates, i.e. natural kaolin from the Merkur quarry, Czech Republic, calcined at 550 °C (metakaolin), raw bentonite from the same region and natural commercially available clinoptilolite from the Nizne Hrabovce deposit (Zeocem, Inc., Slovak Republic), respectively. The adsorption properties and selectivity of prepared sorbents were tested on toxic oxyanions, such as arsenates (As^{V}), arsenites (As^{III}). antimonates (Sb^{V}) and chromates (Cr^{VI}) (Fig. 1). The results showed, that all investigated methods were proper for bentonite treatment, where the sorption efficiency of $As^{III/V}$ varied from 92 to >99 %. In the case of metakaolin, Fe^{III} – treatment was less appropriate thanks to the steric effect of Fe^{3+} hydrolysed particles binding to the surface during the process (FeOOH aggregates are much larger compared to isolated Fe^{3+}particles arising from the Fe^{II} – treatment). The clinoptilolite showed to be a suitable carrier for both the Fe^{II} and Fe^{III} modifications. A less effective Mn^{II} method can be successfully applied in several specific adsorption processes, such as in the competing removal of two similar anions (OUVRARD et al., 2002). The mechanism and kinetics of surface processes depended on the structure of raw material (steric properties, active surface sites), applied treating method and water quality (pH, inicial concentration of anion, competitive ions). The adsorption parameters were calculated by Langmuir and Freundlich adsorption models and by the formal kinetic models. The raw and modified sorbents were characterised by XRD, XRF, SEM, S_{BET}, pH_{ZPC}, particle size distribution, voltametry of microparticles and IR spectroscopy. The characterization of solid phase with above mentioned methods will permit to identify the actual anion-sorbing phases and to tailor the sorbents with the optimal sorption properties.

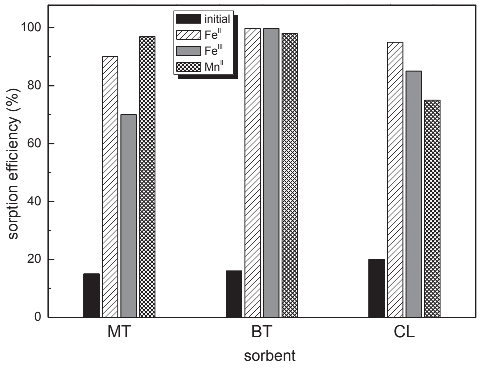

Figure 1. Adsorption efficiencies of raw and modified alumino- silicates. MT – metakaolin, BT – bentonite, CL – clinoptilolite

Acknowledgments

This study was financed by the projects 16-13778S (Grant Agency of the Czech Republic) and TH03030335 (Technological Agency of the Czech Republic).

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Effect of particle shape and surface charge properties on the formation and stability of microaggregates

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Microaggregates form when soil particles connect to larger secondary units. These microaggregates are composed of diverse mineral, organic and biotic materials that are bound together during pedogenesis by various physical, chemical and biological processes. The controlling mechanisms of soil microaggregate formation are not well understood (TOTSCHE et al., 2018). Stable microaggregates in soils are supposed to consist of close associations of Fe oxides and clay minerals with both components being attracted by electrostatic forces between the oppositely charged particles (JOZEFACIUK & CZACHOR, 2014). Soils minerals have very different shapes, particle size distributions and charge properties. Here question arises on possible controls and rules on stable aggregate formation deriving from size and shape as well as the sign and density of surface charge of soil particles. Therefore, our goal was to determine geometrical constraints resulting from particle size and morphology likely impeding optimum arrangement of particles for shielding of charges during aggregate formation.

Aggregation kinetics was determined for nine combinations of each three particle size fractions of goethite and mica in a Zetasizer at pH 6. Experiments were conducted using needle-shape goethites synthesized at 4, 20, and 60°C (lengths of 0.42, 0.46 and 0.84 µm, specific surface areas (SSA) of 87, 75, and 60 m²/g, respectively). As a model for illite ground platy muscovite separated in fine, medium and coarse clay (diameters of 0.16, 0.80, and 2.9 µm, SSA of 182, 100, and 27 m²/g, respectively). Surface charge was quantified by polyelectrolyte titration. The effect of different goethite additions to illite on the zeta potential (ζ) was quantified using an analyzer with phase-analysis light scattering technique (ZetaPALS, Brookhaven). In destabilization experiments by sonication, freeze dried aggregates with mixing ratios representing favorable as well as unfavorable conditions for aggregation were introduced. The particle sizes obtained were evaluated for the decrease of coarse aggregates, increase of particles <0.2 µm, and the shift in mean diameter.

For similarly charged particles a significant tendency for aggregation was observed, easily overcoming the barrier of interaction potential. SEM images of freeze-dried model aggregates confirmed variable size cluster formation of illite and goethite, respectively. Fine illite with in comparison smallest aspect ratio showed strongest aggregation of all size fractions, most probably due to the formation of edge to face structures. The supporting effect of fine muscovite on aggregation of medium and coarse muscovite was lost when its share was <60 %. In heteroaggregation experiments in the muscovite-goethite system marked aggregation was obtained at certain mineral mixing ratios only, where, indicated by zeta potential, optimum shielding of surface charge is given. Within the range of marked aggregation gradients with a zone of maximum aggregation exit. Small and large additions of goethite preserving negative charge or resulting in charge reversal did not have a marked effect on aggregation. Whereas all combinations with fine muscovite facilitated aggregation in a broad range of mixing ratios, inversely the amendment of the fine goethite to medium and coarse muscovite facilitated aggregation at small additions only. Destabilization experiments showed that combinations with preferential aggregate growth have the highest aggregate stability.

The results imply that in soils the aggregation capability of positively charged secondary oxides and negatively charged layer silicates strongly depends on the respective mixing ratio and particle shape and size. As leaching of clay during soil formation primarily affects the <0.2 µm fraction, removal of fine clay can decrease the aggregation tendency.

Acknowledgments
We kindly acknowledge financial support by the Deutsche Forschungsgemeinschaft within the framework of the research unit “MAD Soil - Microaggregates: Formation and turnover of the structural building blocks of soils” (DFG RU 2179).

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Formation of iron-rich phyllosilicates in Si-Fe system in function of Fe/Si molar ratio

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The concept of high and intermediate level long live radioactive waste long-term disposal relies on a multi-barrier system. It involves the presence of various materials between the radionuclides and the environment: glass, steel, cement and a geological formation. At the interfaces between them, interactions may occur that need to be investigated. For example, in France, in the Callovo-Oxfordian (COx) claystone, the interactions with iron at expected conditions have revealed the formation of new phases of phyllosilicates (RIVARD et al., 2015). Among other phases, the precipitation of tri-octahedral serpentine and saponite group phyllosilicates has been described (LANSON et al., 2012; MOSSER-RUCK et al., 2010). In addition, the alteration products of glass in contact with iron are difficult to identify precisely. They look similar to either 1:1, 2:1 or even chlorite iron-bearing clays (SCHLEGEL et al., 2016). The thermodynamic data of these iron-rich phyllosilicates is scarce, limiting the ability to introduce them in geochemical modelling. The objective of this study is to explore the possibility to synthesize iron-rich tri-octahedral clay minerals with tailored chemical composition and structure.

Hydrothermal synthesis was performed at 150°C for 7 days in Si-Fe system with Fe/Si molar ratio varying from 2.33 to 0.50. The X-ray diffraction of oriented slides showed that the 1:1 phyllosilicate synthesis could be achieved with Fe/Si molar ratio corresponding to the theoretical one of 1.50, while 2:1 phyllosilicates could be synthesised with Fe/Si molar ratio ranging from 1.00 to 0.50. Saturation with Ca^{2+} and NH_4^+ revealed that the synthesised 2:1 phases are mixed-layered. The cation exchange capacity of synthesized phases suggested Fe^{3+} substitution in tetrahedral sheet. FTIR analysis confirms the hypothesis of Fe^{3+} located in tetrahedral sheet.

The effects of three parameters, i.e. pH, time and temperature, were explored in order to find optimum conditions for 1:1 phyllosilicate synthesis. As expected, the sample crystallinity improved with time. It is worthy to note that for the same Fe/Si molar ratio (corresponding to 1:1 type phyllosilicate), the maximum synthesis temperature should not exceed 150°C. The pH variation was observed during the different synthesis steps and its adjustment during the preparation of the precursor caused important variations in the volume of the precursor solution therefore, the choice was made to fix the OH^-/Fe molar ratio in the mixture. It was shown that a molar ratio between 2 and 3 leads to the formation of a 7 Å phase.

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Influence of clay mineralogy for heavy clay products

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The production of fired bricks started in the ancient age. The technology has been the same for more than two thousand years. With the beginning of the industrial age in the 19th century an evolution of engineering, equipment, controlling and natural science took place. Therewith a wider range of raw materials was possible. But the specifications, for instance a constant homogeneous brick body, have increased to higher levels. And the dispute about clayey raw materials like an object of investigation has begun. In former time simple and empirical knowledge was good enough. Then the focus has changed to systematical analysis. The analysis results are necessary for planning, building and operating brick plants. For controlling production and quality this is also important.

Natural raw materials for heavy clay products are multicomponent systems of several clay- and non-clay minerals. They are sediments, loose or consolidated. Depending on their composition different products are possible and various ceramic-technology behaviours are measurable. The main influence comes from the kind and amount of clay minerals. Structure, phase content and chemical composition are essential parameters of the raw materials. The structure is defined by the grain size distribution while the phases are identified with mineralogical analysis. With increasing consolidation the level of treatment has more and more influence on granulometry. However, the topic of this contribution is mineralogical composition of clayey raw materials.

State of the art is the X-ray diffraction analysis. The method used in our institute is powder diffraction of whole sample and of clay mineral fraction. This fraction is separated, for better characterisation. The measurements take place in typical Bragg-Brentano geometry, reflection mode. Transmission mode is used infrequently. Quantifications are made with external and internal standard methods with Rietveld computing. Additonally, thermal analysis is commonly used. The residues from wet sieving are also analysed.

Common clay minerals in raw materials for brick manufacturing are smectite, illite-smectite mixed layer (I-S), illite, disordered kaolinite, kaolinite, chlorite and mica. Other clay minerals have no significance, or are important in some localities only. Some important effects of different clay minerals are:

smectite:	plasticity, sensitivity while drying, dry bending strength, shrinkage, resorption of humidity
I-S:	same like smectite and strength of fired ceramic body
illite:	plasticity, texturation of extruded body, sintering of ceramic body
disordered kaolinite:	plasticity, texturation of extruded body
mica:	grog of plastic body, flux with higher firing temperature
chlorite:	in loose raw material: plasticity; higher firing temperature needed
kaolinite:	plasticity, not sensitive while drying, low dry bending strength, resistance against deformation during firing process, higher firing temperature needed

A useful first arrangement is sorting clayey raw materials to loam, clay and marley clay. This is not a sorting by geological genesis. Commonly all loams in central Europe contain smectite, illite, mixed layer, disordered kaolinite, mica and in rare cases chlorite, e.g. around the Alps.

Clays can be graded by their main clay mineral. This determines the ceramic-technology properties. For instance, illitic clays make a dense ceramic body by lower firing temperature. In the north of Germany there are interglacial basin clays. It is difficult to sort them after one characteristic clay mineral since more than one clay mineral is dominant. Kaoline is a special case of kaolinitic clays. They have an impact on products with higher firing temperature only, like clinker bricks.

Marly clay is characterized by higher content of carbonate minerals, like calcite and dolomite. They impact temper of plastic brick bodies during extrusion process. Because of the decomposition of carbonates during firing the products have a higher porosity. Therefore such raw materials are main component for wall bricks with better thermal insulation. Clay minerals we can find are smectite or I-S rather than disordered kaolinite and chlorite. A special case is the use of carbonate smectite clays for roofing tiles, which are usually not used due to the fact that the frost-resistance with this raw material is very difficult to accomplish, in the Mediterranean region for roofing tiles.

9th Mid-European Clay Conference – MECC 2018

Preliminary attempt to define grade of diagenesis and incipient metamorphism considering geothermal gradients calibrated with clay mineral, mineral and maceral index data

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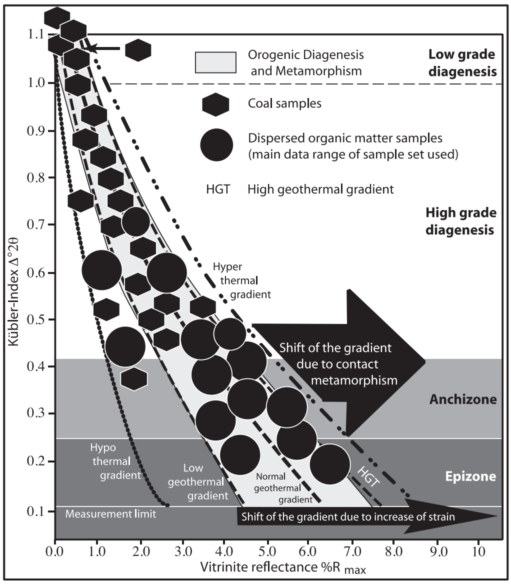
Comparing the samples from coal basins (Saar, Ruhr, Appalachian, and Petrosani), Alpine and Variscan Molasse basins and inverted tectonic settings in mountain belts (folded Molasse, Austroalpine, Helvetic Alps, Penninic units, South Carpathians, Stara Planina, Taurus mountains, Franciscan complex, Caledonia, Hikurangi prism) it is striking that illite Kübler Index (KI), chlorite Árkai Index (AI), mineral and clay mineral paragenesis and maceral reflectance data show different correlations. These differences define different relations for hypothermal, normal thermal and hyperthermal heat flow conditions (geotherms, Fig. 1) thus allowing a translation to geothermal gradients (Fig. 2). The correlation with AI and vitrinite like solid bitumen (VlB) reflectance is not shown, both corroborate the results of the figures.



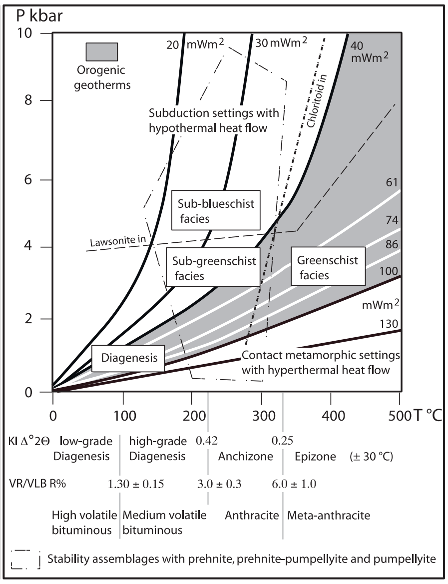


Figure 1. (left) shows the relations found in geodynamic settings studied by sample sets used for the correlation shown in Fig. 2. (right). The location of the coal and dispersed organic matter samples is plot on the KI versus vitrinite reflectance %R_{max} (VR) graph. Ranges of orogenic thermal gradients (light grey area) with the limiting low and high geothermal gradient as also the moderate gradient (given as the normal geothermal gradient) are shown. The outer reference lines indicate shifts to hypothermal (subduction tectonics) and hyperthermal (extensional tectonics) conditions. Contact metamorphism causes strong local shifts to higher VR values as also the increase of strain in the high-grade anchizone and epizone.

Figure 2. (right) The figure presents a rough correlation of the Winkler pressure (P)-temperature (T)-diagram with KI, VR %R_{max}, and VlBR %R_{max}. The KI decreases in precision when correlated with VR. The subdivision of grade of diagenesis shown in both graphs uses the limiting VR for the high volatile bituminous and medium volatile bituminous boundary (see also the anchizone/epizone versus anthracite/meta-anthracite stage correlation). The mineral stability assemblages of prehnite and pumpellyite and the reaction isograde of lawsonite and chloritoid are used to define limits of low-grade metamorphic facies.

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Impact of mineralogy and pore water chemistry on the CEC of the Boom Clay (Belgium)

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In the context of the disposal of radioactive waste, the Boom Clay in northern Belgium has been studied intensively for the past decades as a potential host rock. One of the parameters of interest is the cation exchange capacity (CEC), as it is related to the sorption potential of radionuclides to the clay host rock. In the past, a number of studies have been performed to assess the CEC of the Boom Clay. The results of these studies were not comparable due to variations in methodology and the limited number of samples being used (HONTY, 2010).

Our study attempts to settle the ambiguity by addressing these problems by (a) collecting a stratigraphically diverse sample set and (b) using a standard methodology. A sample set covering the entire Boom clay stratigraphy was assembled, after which the CEC was determined. The copper (II) triethylenetetramine method with calcite saturation (DOHRMANN & KAUFHOLD, 2009) was chosen to prevent the dissolution of carbonate minerals. The main sample set was also measured with the cobalt (III) hexamine method with calcite saturation (DOHRMANN & KAUFHOLD, 2009) as a quality control for the results of the former method. The CEC values acquired with both methods are similar, while a significant stratigraphical variation of the CEC is demonstrated. These variations could be linked to variations in the clay mineralogy.

In addition to constraining the CEC, the exchangeable cation population of the Boom Clay was assessed for the first time. These data were then compared to *in-situ* pore water chemistry to uncover possible relations between the pore water and the exchangeable sites of the clay minerals. The exchangeable sodium content was found to be correlated to the pore water sodium concentration, which provides evidence of mixing with meteoric water, a theory which was put forward by MAZUREK et al. (2009).

Acknowledgments

The authors would like to thank NIRAS-ONDRAF, the Belgian Agency for Radioactive Waste and Fissile Materials, for providing the clay cores on which the study was executed.

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Recycling of rare earth elements from electronic wastes by selective adsorption on industrial clay minerals

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The REEcycling project investigates the adsorption of rare earth elements (REE) on bentonites. The aim is to use the adsorption mechanisms of smectite-rich clay mineral fraction for the extraction of REE in hydrometallurgical processes. Previous studies have shown that the raw materials used are generally suitable for extracting REE ions from multi-elemental solutions and that the adsorbed REEs might be removed by the clay minerals by a strong reduction of the pH-value.

The processing and chemical pretreatment of the raw materials is important. Various benefication processes like grinding and sieving are used for this purpose, as well as a preliminary chemical leaching of the raw materials using acids. The aim is to generate the highest possible cation-exchange capacity (CEC) from the available raw materials with economically viable means.

The adsorption process itself was studied using a suspension of REE containing standard solutions and several clays. The standard solutions were produced from a mixture of different ions, which are based on real hydrometallurgical solutions. After the reaction the REE-enriched clays were separated and further processed to retrieve the adsorbed REE. The entire process of adsorption and desorption was strongly depended on the pH value.

The aging of the clay minerals after several adsorption and desorption cycles was evaluated with several analytical techniques, which include chemical analyses, XRD, CEC measurements, optical methods and the determination of the BET specific surface area. The long term stability of smectites in several acidic solutions is a major part of this project.

The results of this project display new applications for specific clay minerals and a cost effective highly selective possibility to remove REE out of hydrometallurgical solutions without contaminations from other elements.

Acknowledgments
The project is supported by the German Federal Ministry of Education and Research. Grant reference: 033RK042B

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Use of SWIR spectroscopy for the exploration of permeable fracture zones in geothermal wells exploiting a deep-seated granite reservoir

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The fracture zones (FZ) in the granitic basement of the Upper Rhine Graben (URG) are bearing the major permeability (GENTER et al., 2000). The Rittershoffen (Alsace, France) heat plant initiated in 2004 is composed of two deep-wells (GRT-1 and GRT-2) producing a natural brine at 168°C on surface with a production flow rate of 70L/s pumped from a deep fractured granite reservoir associated to the normal fault of Rittershoffen. Intense structural and mineralogical studies of these two wells were performed in order to characterize permeable FZ (VIDAL et al., 2017, 2018). X-ray diffraction results indicate that the occurrences of poorly crystallized illite and mixed layers illite-smectite (ml I-S) (<10 % smectite) were systematically and spatially linked with the occurrences of permeable FZ and thus provide specific clay signatures for FZ (Fig. 1) (VIDAL et al., 2018). In this study, we propose an innovative method to detect highly clayey zones corresponding to permeable FZ developed in crystalline rocks using short wave infrared (SWIR) spectroscopy. It is a common technique for field exploration in the mining industry since it is rapid and non-destructive but remains poorly applied in geothermal exploration. SWIR spectra were acquired for more than 900 cuttings samples in the granitic section of the two Rittershoffen wells. In the GRT-1 well, the SWIR results correlate with the XRD results and the former binocular loupe observations having identified several granitic facies. The total area of absorption bands yields specific values for different granitic alteration facies. More precisely, a sound granite shows values under 20, an extremely altered granite (HEXT) shows values around 30, as moderate and low altered granite (HMOD and HLOW) show values comprised between 20 and 30 (Fig. 1). In a permeable FZ, the area of the Al_2OH band increases from 2330 to 2370 m Measured Depth (MD) and seems to correlate with the increase of illitic minerals amount at these depths. Inside the FZ, the increase of H_2O band area from 2330 to 2350 m MD suggests an increase of the quantity of all clay minerals in the altered damage zone (HEXT facies) of the FZ (Fig. 1). In the core of the FZ, the decrease of H_2O band area from 2350 to 2370 m MD suggests a low quantity of clay minerals that correlates the occurrences of quartz vein (VEIN facies) (Fig. 1). The data analysis will be extended to the second geothermal well GRT-2. Using field SWIR spectroscopy could be a convenient method to monitor the forthcoming drilling operations for future geothermal wells located at Illkirch (Strasbourg area, Alsace) that will start in June 2018.

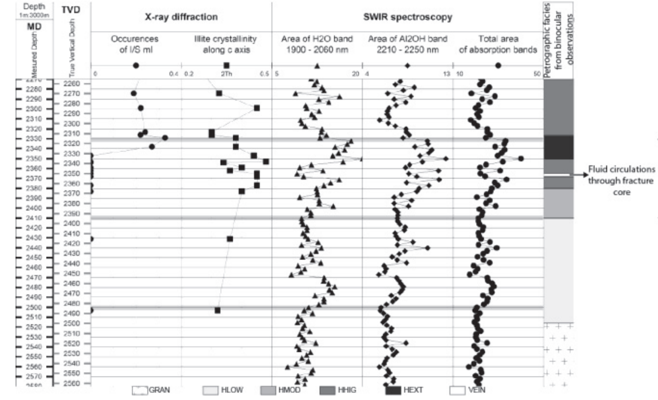

Figure 1. Composite log of the GRT-1 well with X-ray diffraction results, the SWIR spectroscopy and the granitic facies.

Acknowledgments

This work was undertaken in the framework of the EGS Alsace project, which is co-funded by ADEME, the ÉS group and EOST. This work is based on ECOGI project data as a contribution to the PhD thesis of Carole Glaas, which is co-funded by ANRT (French Research and Technology Agency) and ÉS-Géothermie.

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Pore-scale processes in clay-bearing chalks: an example from the Outer Carpathians (Poland)

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Geological history of sediments is recorded in pore-scale processes, and these phenomena influence petrophysical properties of rocks the most. Due to limited permeability, pore-scale processes occurring in fine-grained rocks are particularly diversified and localized in contrast with other types of rocks. Fine-grained calcareous rocks of an impure chalk type were chosen for this study. The clay component of these rocks is thought to be a key factor, which is critical for development of sealing or reservoir properties of these rocks.

This study focuses on imaging of pore space and the relationships among clay and the other components of impure chalk in order to decipher post-sedimentary processes influencing the porosity evolution in these rocks. The impure chalks, which are called marls in the Outer Carpathian region (GÓRNIAK, 2011), were studied. Marls, showing variable amounts of carbonates, clay, and silica minerals have been selected (GÓRNIAK, 2017a). The following types of marl matrix were analyzed: (1) carbonate and clay supported (Grybów Marls, Tertiary, Fore-Magura Units); (2) carbonate, clay and silica bearing (Jasienica Marls, Upper Cretaceous, Sub-Silesian Unit); (3) carbonate-silica supported (Sub-Cergowa Marls, Tertiary, Dukla Unit); (4) clay-dominated (Frydek Marls, Upper Cretaceous, Sub-Silesian Unit); and (5) clay-silica supported (Budzów Marls, Tertiary, Magura Unit) (GÓRNIAK, 2017b). X-ray diffraction, field emission gun scanning electron microscopy, thermal analysis, chemical analysis and helium porosimetry were used to solve the problem.

The data obtained are as follows: (1) clay in the rocks studied is strongly dominated by illite-smectite (I-S); (2) subordinate clay component in organic matter-rich marls is kaolinite; (3) the appearance of I-S is both detrital and authigenic whilst kaolinite is exclusively authigenic; (4) the content of clay varies from 28-53 % and the proportion of carbonate to clay and silica ranges from 1.0:6.0:0.1 to 1.0:7.0:3.0; and (5) the porosity of the different varieties of marls range from 0.11-16.82 %.

The following pore-scale processes, in which clay was involved, have been recognized as occurring in this order: (1) mechanical compaction documented by deformed clay aggregates; (2) localized cementation proven by the presence of coccolith clusters; (3) localized dissolution confirmed by disarticulated coccoliths; and (4) formation of authigenic clay, which ultimately clogged pore spaces.

The study revealed that: (1) the reduction of porosity is not dependent only on clay content, but also on the presence and content of silica minerals; (2) the proportion of clay to calcite is not a deciding factor; (3) the distribution together with the content of clay, carbonate and silica minerals are the key factors, which influence porosity; (4) the pore-scale processes which took place throughout the history of the formation of the rocks studied is dependent on the composition of the starting material; and (5) the clay present in the rocks studied can be interpreted as intra-basinal component, which shows detrital appearance due to re-depositional processes.

Acknowledgments

Funding provided by the Grant no 11.11.140.158 of the AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection.

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The stability of bentonites in aqueous solutions (25 to 120°C) relevant to the underground sealing of radioactive waste deposits

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Bentonites generally vary in their physical and chemical behavior largely due to the types of smectites present as well as the differences in the accessory minerals (e.g presence of pyrite, carbonates, feldspars). Although bentonites have been generally well studied, their suitability as effective long-term seals for underground radioactive waste disposal remains a topic of debate. We present results on the mineralogical and geochemical changes of selected bentonites subjected to aqueous solutions that simulate i) Opalinus shale pore waters and ii) alteration of a gypsum-seal in a salt diapir (NaCl-$CaSO_4$-saturated) at temperatures between 25°C and 120°C. These conditions are relevant to the underground disposal of nuclear waste. Most of the barrier materials studied have been well characterized both mineralogically and chemically (UFER et al., 2008) and have been shown to have a broad range of clay mineral stabilities (e.g. KUFHOLD & DOHRMANN, 2010). The aim of this work is to assess the controlling mechanisms that lead to alteration of bentonites and to determine which bentonites show the highest degree of stability under repository conditions. Using laboratory batch experiments, changes are monitored using a broad range of analytical data. Overall, our results confirm that bentonites do display a broad range of stabilities when subjected to shale pore waters or saline-$CaSO_4$ solutions. CEC and bulk mineralogy change minimally at lower temperature while calcite is being reduced at higher temperatures. Carbonate minerals seem to play a major role in the pH development, although the pH stays fairly constant in samples that contain more than 0.5 wt% calcite. During the dissolution of calcite, CO_2 is released and pressure builds up at 120°C, with some CO_2 possibly originating from the interlayer of the smectites. Some significant loss of the ability of smectite to swell is also observed at higher temperature based on XRD patterns. Fe mobilization is evident visually and chemically possibly due to the oxidation of pyrite. The source of the mobilized Fe and its role remains to be determined. The overall relevance of these results will be discussed in the context of bentonite barriers stability, and the discussion will include the role of microorganisms that are fertilized in some batch experiments.

Acknowledgments

This study was financed by BMWi (FKZ 02E11344C).

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Investigation of the surface sites of tubular halloysite using phosphate anions

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Over the last 20 years the interest in halloysite has increased dramatically and these non-toxic and biocompatible nanotubes have found novel uses as components in polymer composites, adsorbents for decontamination purposes, batteries, flame retardant materials and drug delivery systems, to name but a few. This project aims to investigate the adsorption sites of two tubular halloysites of different morphologies (Figs. 1 and 2) by using phosphate anions as a probe in adsorption and desorption reactions with varying pH's and background electrolyte ionic strengths. Furthermore, a series of kinetics experiments were also conducted.

The mechanism of adsorption and desorption has also been hypothesised using a combination of analytical techniques such as Fourier Transform Infra-Red (FTIR) and atomic force microscopy (AFM). Surface complexation modelling will be applied in an attempt to confirm the observed experimental results.

A key significant finding of this study is that the type of tubular halloysite has a definite effect on the anion adsorption capacity where the cylindrical type tubes have around 2.5 times greater maximum adsorption than the polygonal prismatic tubes. While it is shown that changes in the background electrolyte strength have minimal effects on the adsorption of phosphate, pH, as expected has a significant effect and maximum adsorption for both halloysites is seen around pH 6. Initial findings from the kinetic experiments have indicated that the maximum adsorption is obtained in less than 48 hours and adsorption remained constant from this time up to a period of ten days.

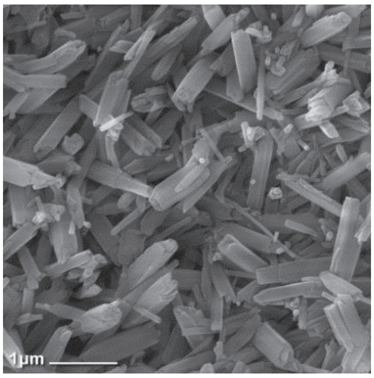

Figure 1. Polygonal prismatic halloysite nanotube (HILLIER et al., 2016).

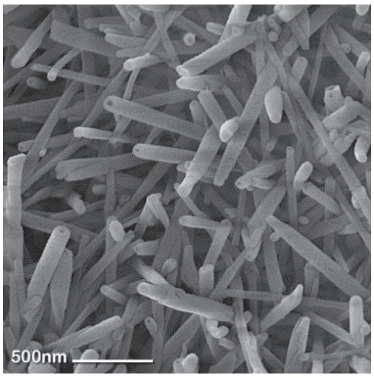

Figure 2. Cylindrical halloysite nanotube (HILLIER et al., 2016).

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Roman pottery workshops in the province *Dalmatia*: identifying clay sources and production technology through mineralogical analysis

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Several pottery workshops and seemingly isolated kilns dated to Roman times have recently been identified in the coastal area of province *Dalmatia* (eastern Adriatic), more precisely in its northernmost part, ancient *Liburnia*. Within a programme of archaeometric analysis[1], mineralogical characterisation of clays and pottery samples was carried out in the attempt to identify clay sources utilised for pottery production and determine the temperatures of firing. For this purpose, samples of production waste from four kiln sites (Crikvenica, Plemići bay near Ražanac, Podšilo and Mahućina bays on Rab Island) were compared to potential clays sourced in the vicinity of the sites.

Mineralogical analysis of clayey materials included X-ray powder diffraction (XRPD) on pottery samples and clayey materials. Clayey materials were also analysed on random mounts of bulk samples and oriented mounts of the <2 μm fraction. Oriented mounts of the <2 μm fraction were recorded after the following treatments: a) air drying, b) saturation with K^+ and Mg^{2+}, c) ethylene-glycol solvation, d) heating to 400°C and 550°C. The determination of the pottery firing temperature included drying modelled clayey materials at room temperature for 4 days and firing at temperatures ranging from 700 to 850°C.

The mineralogical analyses showed that the main mineral components of all clayey materials are quartz, swelling clays and illite/muscovite. Calcite is present in samples from Crikvenica and Plemići. Among the swelling clays smectite is dominant in samples from Crikvenica, Plemići and Podšilo, while vermiculite is dominant in samples from Mahućina. Feldspar and kaolinite are present in a lesser quantity in all samples, while chlorite is present only in some samples. Quartz is the main mineral which is regularly present in all pottery samples. Pottery samples together with quartz also contain some of these minerals: illite/muscovite, calcite, feldspar, hematite and clinopyroxene.

Results point out that in some cases the clays collected from sources identified in the sites environs could have been utilised in pottery production and the mineralogical composition of clays and pottery sherds helped identifying the possible firing temperatures. Thus, results offer a valuable insight into facilities' installation choices, production organisation and technology.

Acknowledgments
This contribution and the analysis carried out are activities of Project RED - Roman Economy in Dalmatia: production, distribution and demand in the light of pottery workshops (HRZZ, IP-11-2013-3973).

Clay mineralogy of soils developed on Miocene marl sections of Mt Medvednica, NW Croatia: Origin and transformation in temperate humid climate

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Clay mineralogy of marl deposits and overlaying soil horizons (rendzina and brown soils after ŠKORIĆ, 1977; BOGUNOVIĆ et al., 1996) was investigated in the southeastern foothills of Mt Medvednica, Croatia. The marl was deposited during Miocene ages in various depositional environments (saline, brackish and fresh water). The overlaying soil profiles are poorly developed with A and C horizons usually present. C horizon is developed as a transitional horizon towards the underlying rock and often contains rock debris. Altogether nine marl-soil sections were investigated for discrete changes in clay mineralogy among and within sections.

The mineral composition of the bulk samples was determined using X-ray diffraction (XRD). Carbonates, organic matter and Fe-Mn oxyhydroxides were chemically removed to separate clay mineral fraction. The residual was centrifuged and clay fraction was extracted for preparation of oriented mounts. The oriented mounts were air-dried, glycolated and heated at 400 and 550°C for half an hour, and in each step analyzed by XRD. As indicated by the position and shape of 10 Å peak, illite is present in all the samples. The varying constituents are smectite and interstratified illite/smectite. A regular pattern of occurrence was observed: pure smectite never occurs in the topsoil and is present in the transitional horizon and underlying rock. Interstratified illite-smectite is always present in the topsoil, and sometimes also in the underlying horizons. Smectite and illite-smectite were mutually distinguished largely by their behavior after glycolation Illite/smectite is randomly interstratified with illite component reaching maximally 30 %, mainly in A horizon. Distribution of these two minerals seems to be mostly governed by stratigraphic position, topographic outline, and soil profile development. Chlorite and kaolinite are present as minor constituents in majority of the samples with exemption of the sections related to Lower Miocene marl deposits. Kaolinite is generally not present in the marl horizon of any section.

Cation exchange capacity was determined using copper(II)-ethylenediamine complex. The results show a significant change of values upon removal of non-clay components from marl and especially soil. Two trends can be generally observed: a) in the bulk samples CEC values decrease with depth, and b) in the separated clay fraction CEC values increase with depth. For the bulk samples the CEC values are the highest in horizon A which is the only horizon with decreasing CEC values after removal of non-clay components. This indicates a strong contribution of organic matter to the bulk CEC values in top-soil horizon (SILVEIRA et al., 2002; VEGA et al., 2007). The increase of the CEC values with depth in clay fraction implies higher quantity of clay minerals with higher adsorption capacity; in this case it can be related to the increase of smectite phase or smectite component in illite-smectite. Additionally, deblocking of adsorption sites due to the removal of Fe-Mn-Al oxyhydroxides also could play a role (WU et al., 1999). The measured CEC values correspond well to the observed clay mineral composition of the samples.

The bedrock marls contribute as a source of expandable clays in overlying soil horizons. However, a portion of them could have been formed by transformation of other inherited clay minerals like illite or by precipitation from soil solution. The neoformation could be supported by slightly alkaline pH due to the presence of carbonates, an increased Mg activity provided by dissolution of carbonates, and poor drainage of the marl terrains (REID-SOUKUP & ULERY, 2002).

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Palaeoenvironmental reconstruction of a Permian playa lake: the Boda Claystone Formation

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The study of the Boda Claystone Formation - one of the potential host rocks for radioactive waste disposal - and of its geological environment, the Western Mecsek Mts. dates back to several decades. To decide on the location of the suitable disposal area, a detailed knowledge on the geology of the formation is necessary. The depositional environment of the Boda Claystone Formation is still unclear, and the recent ideas contradict each other. Clarification of these issues is necessary for the palaeoenvironmental reconstruction.

The investigated sediments were deposited simultaneously with the end of the Permo-Carboniferous (Karoo) ice age. The Permo-Carboniferous ice age (ROSCHER & SCHNEIDER, 2006) was followed by warmer climate, during the Late-Permian the climate became dryer on the Northern Hemisphere (SCHENEIDER et al., 2006). The palaeoclimate reconstruction of the Sakmarian and Wordian age was made by the distribution of climate indicator sediments, mainly paleosols (CHANDLER et al., 1992). SCOTESE (2001, 2002) also suggest arid/semiarid climate on his paleoclimate map of the Boda Claystone sedimentation area. Clarification of this idea was done by detailed investigation on paleosols, where the homogeneous red clays indicates dry events under similar condition.

Our results have been achieved by geological, geophysical data and methods, and partly by geoinformatics applications. We have clarified the cyclostratigraphic results of the Permo-Triassic successions. We elaborated a methodology for the interpretation of the cyclicity in the succession, which was applied on Ib-4 borehole, then the whole succession was investigated. We also carried out a colour-based analysis of homogeneous rocks, mainly on clays, which proved the usability of the facies analysis. By analysing geophysical data, we have been able to clarify the cyclicity of the clay succession. It was possible to find the relationship between the fourth and fifth order cycles of the Boda Claystone and the ratio of the Milankovitch cycles 1:2:4.8 (21,000, 41,000, 100,000 years) also appear in the thickness of the lower order cycles (assuming a uniform sedimentation rate).

Red clays are typically paleosols in the succession, which, according to the literature can be associated with arid/semiarid climate. The silty claystones, which compose the major part of the sequence, lost their primary structures due to pedogenic processes and indicate prolonged subaerial intervals with soil formation and only ephemeral inundations. The presence of pedogenic carbonate concretions supports the interpretation of an arid climate and a relatively shallow groundwater table. To clarify this question, micromorphological studies were done, as well as the reinterpretation of the large number of available thin sections. Based on our investigation, the paleosols developed near or in the playa mudflat, where it meets (interfingering) with the alluvial debris sediments.

Acknowledgments

This study was partly financed by PURAM Ltd., Mecsekérc Ltd. and UP.

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Stability of Fe-containing minerals in the oxidized zone of the Boom Clay

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In the context of radioactive waste disposal in clay formations, the sorption of a number of long-lived radionuclides (e.g. U, Se, Tc) is controlled by the presence of Fe-containing minerals, mainly illite (BRUGGEMAN et al., 2010), smectite (GUIMARAES et al., 2016) and pyrite (BREYNAERT et al., 2010). During oxidation events, e.g., caused by the excavation and ventilation of galleries, the redox state and/or sorption properties of these minerals may change in the near field with possible formation of secondary minerals. The objective of this study was to evaluate mineral stability of the Boom Clay (BC) in the oxidized zone with a special focus on Fe-containing minerals.

For this purpose, thin slices (2-5 mm) of two sample series over a distance of 40 cm from the Test Drift (TD, 20 years old) and the Connecting Gallery (CG, 7 years old) located within the HADES underground research facility (Mol, Belgium) were investigated by XRD, FTIR, XANES, Mössbauer spectroscopy, CEC-Cu-trien (MEIER & KAHR, 1999) and leachate chemistry.

In both series, the iron occurs as trivalent atom in the octahedral sites of illite and illite-smectite, whereas divalent Fe is attributed to pyrite. Radial pyrite content profiles along boreholes drilled from HADES show that pyrite is more abundant in the clay around the TD than around the CG but its relative content decreases towards the galleries in both sample series. Pyrite oxidation is also reflected in the increased sulphate concentrations in the leachates compared to undisturbed pore water, with relatively higher values in the leachates from the CG samples compared to the TD samples. Gypsum was found as an alteration product in both sample series, but jarosite is found exclusively in the CG samples. The precipitation of jarosite is interpreted as a local phenomenon associated with the complete dissolution of carbonates and subsequent loss of buffering capacity at low pH. Over a longer period, jarosite stability might be affected by the buffering role of the concrete lining and/or buffering of the BC pore water draining towards gallery.

CEC varies between 18-24 cmol$^+$/kg in the samples from the CG and between 15-21 cmol$^+$/kg in the TD. These ranges overlap with a reference CEC value of 21±1.5 cmol$^+$/kg for undisturbed BC at the depth of the HADES facility (ZEELMAEKERS et al., 2015). Although there is a decreasing trend in the CEC observed towards the gallery in both sample series, most of the variations remain within the uncertainties of the applied method. Therefore, we can conclude that oxidation does not have a significant impact on either the stability of Fe-phyllosilicates or the cation exchange capacity of the BC in the studied case.

Acknowledgments
This work is performed in close cooperation with, and with the financial support of ONDRAF/NIRAS, the Belgian Agency for Radioactive waste and Fissile Materials, as part of the programme on geological disposal of high-level/long-lived radioactive waste that is carried out by ONDRAF/NIRAS.

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Genesis of the Yarıkçı hydrothermal kaolinite deposit within Paleozoic metamorphic units, Mihalıççık, Eskişehir, Turkey

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The kaolinitic claystone of the Yarıkçı deposit (Eskişehir, central Anatolia) is an important source of raw material for tiles and glaze. No detailed genetical and geochemical studies of this deposit have been carried out to date. The aim of this research is to fill this knowledge gap. Hydrothermal alteration developed within Paleozoic metamorphic units along NW-SE trending normal fault zone at the study area are the main reason for formation of kaolinite deposit (SİNCAN, 1979). The mineralogical and geochemical characteristics of 52 fresh and altered samples were examined using polarized-light microscopy, X-ray diffractometry (XRD), scanning-electron microscopy (SEM-EDX), and chemical (ICP-AES and -MS) methods. The kaolinitic claystone units include abundant iron oxide and silica phases that have either filled fractures and stockwork or stained the kaolinitic units. Kaolinitic claystone is hosted by chlorite schist, chlorite muscovite schist, muscovite schist and talc schist, composed of altered muscovite, chlorite, plagioclase and K-feldspar associated with quartz, calcite and talc showing cataclastic texture due to tectonic activities. These units are covered by hard, dark, sharp edged thick silica cap. The claystone shows white, green and brown colors related to abundance of kaolinite±smectite±opal-CT, smectite±kaolinite±iron oxide, smectite±iron oxide phases, and hematite/goethite. Micromorphologically, kaolinite typically has a platy form with irregular margins and locally a subrounded vermiform texture in finer euhedral kaolinite crystals suggesting formation in several phases. The association of gypsum/sulfur, iron oxide and opal-CT/quartz, jarosite, and microorganism is indicative for influence of hydrothermal activities and acidic environmental condition (MEUNIER, 2005). Local increase of SiO_2, Fe_2O_3, S, Cu, and Au concentrations also support this suggestion. High values of Sr, Rb, Ba and Zr reflect volcanogenic while Cr_2O_3, Ni and V reflect ophiolitic contributions. Development of iron oxide minerals on kaolinite plates and as films on siliceous material indicates injection of iron oxides during/following kaolinization and silification process. The slight to moderate depletion in Light Rare Elements (LREE) compared to the Middle (MREE) and Heavy REE (HREE) and positive Eu and negative Ce anomalies normalized to the PAAS values are responses to the fractionation of feldspar by the hydrothermal fluids (HRISCHEVA & SCOTT, 2007). The close association between kaolinite plates with feldspar, smectite, and muscovite suggest that kaolinite formed from feldspar, volcanic glass, smectite and muscovite by dissolution under acidic condition. Illite also developed at the margins of smectite plates via dissolution-precipitation mechanism under alkaline conditions.

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Geology, mineralogy, geochemistry and genesis of bentonite deposits in Miocene volcano-sedimentary units of the Balıkesir region, western Anatolia

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The widespread Balıkesir bentonite deposits within the Miocene volcano-sedimentary units in western Anatolia have economical potential; they are important source of raw material for the ceramics industry in Turkey. The mineralogical characteristics of 71 samples from these bentonites and their host rocks were examined using polarized-light microscopy, X-ray powder diffractometry (XRD), differential thermal analysis and thermal gravimetry (DTA-TG), scanning and transmission-electron microscopies (SEM-EDX and TEM), and chemical (ICP-AES and -MS) methods. In the bentonite deposits smectite, associated with smaller amounts of illite, quartz, feldspar, dolomite, calcite, and opal-CT, is the most abundant clay mineral. The well-ordered smectite was identified by sharp basal reflections at 14.42–14.93 Å, sharp infrared spectral bands and the characteristic smectite reaction to heating. Plagioclase and sanidine crystals in volcanic units are altered and sericitized, biotite and hornblende are partly to completely opacitized and chloritized. Micromorphologically, smectite flakes occur on altered feldspar and mica grains and devitrified volcanic glass fragments in association with or without calcite±dolomite crystals. Increasing Al+Fe+Mg/Si ratios with increasing degree of alteration reveal that hydration of volcanogenic grains (feldspar, mica, hornblende, glass shard) by chemical weathering was the main controlling mechanism on precipitation of montmorillonitic smectite, with average structural formula of $(Ca_{0.30}Na_{0.03}K_{0.04})(Al_{2.74}Fe_{0.17}Mg_{1.27})(Si_{7.99}Al_{0.01})O_{20}(OH)_4$. Enhanced Ba, Sr, Zr values and increase of LREE/HREE ratio, together with a distinct negative Eu anomaly show that the Si, Al, Fe, and Mg required to form smectite were probably supplied from the decomposition of feldspar, amphibole, and volcanic glass from volcanic units (ZHOU et al., 2013). The positive correlations between the Zr/Ni and Zr/Co ratios, and Rb+Ba and Na_2O+K_2O suggest that smectite formed from volcanic materials during chemical weathering processes (GHANEM & JARRAR, 2013; MOTOKI et al., 2015). Variable La/Yb, Nb/Ta and Zr/Hf ratios from the different bentonite deposits in the study area may also reveal different volcanic sources. Association of carbonate rocks within the smectite-rich clayey rocks, absence of chlorite and detrital materials such as rock fragments in the bentonites suggest that the bentonite deposits formed as “primary bentonites” from volcanoclastic materials deposited in a calm lacustrine environment during an early diagenetic weathering process (JEANS et al., 1982; KADİR et al., 2017).

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About the relation of tetrahedral Fe, tetrahedral charge, and Fe-content of dioctahedral smectites

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The tetrahedral charge of dioctahedral smectites commonly ranges from 10 to 60 % (few exceptions exist). Many authors identified a positive correlation of both parameters according to which the tetrahedral charge of dioctahedral smectites increases with increasing Fe-content (WEAVER & POLLARD, 1975; BADRAOUI & BLOOM, 1990; BUJDÁK et al., 2001; RYAN & HUERTAS, 2009; WOLTERS et al., 2009). The aim of the present study is to investigate the reason for the existence of this correlation. Kaufhold et al. (2017a) considered the role of tetrahedral Fe in this respect. A positive correlation of tetrahedral iron and tetrahedral charge was postulated. This hypothesis would lead to a kind of distribution coefficient (e.g. 1/10 of total Fe is found in tetrahedral coordination). Spectroscopic studies on selected samples, however, proved that no such distribution coefficient exists. Some samples with low iron content had some of its few Fe in tetrahedral coordination and others which were rich in Fe did not show any Fe in the tetrahedral sheet. This hypothesis, therefore, was rebutted. The same authors then suggested a model according to which waters penetrating through Fe-rich (alkaline) volcanic rocks in which smectite formation is active are supposed to be more alkaline than in more acidic (Al-rich) rocks. The higher pH of waters in alkaline rocks in turn leads to tetrahedral coordination of Al in the solution and hence can be better incorporated into the tetrahedral sheet. An alternative explanation could be derived from energetical considerations. It could be possible that Fe in the octahedral sheet would favor Al to be incorporated in the tetrahedral sheet. These correlations, along with the phenomenon that the type vacancy (either cis- or trans-vacant) is also correlated with the Fe-content, were investigated based on quantum chemical density functional calculations (KAUFHOLD et al., 2017b). The empirically determined and well known structural correlations of dioctahedral smectites (Fe-content vs. tetrahedral charge; Fe-content vs. trans/cis-ratio; tetrahedral charge vs. trans/cis ratio) could be traced back to energy relations. In conclusion, a larger content of octahedral Fe facilitates the substitution of Si by Al in the tetrahedral sheet. At the same time trans-vacant positions become favorable. A few samples (<5 %), however, were identified which do not follow the trend which points to the existence of “common” and “uncommon” smectites.

Acknowledgments
The study is a summary of results published by KAUFHOLD et al. (2017a) and KAUFHOLD et al. (2017b). All Co-authors are acknowledged for their valuable contribution.

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Combined ab initio and XAFS spectroscopy study on the characteristics of metal uptake by clay minerals

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Clay minerals can bind transition metals under mildly acidic to basic pH conditions. Their ability to retain radionuclides is extensively used in various concepts for the geological disposal of high level radioactive waste (HLW). In the Swiss concept, spent fuel (SP) and vitrified HLW will be encapsulated into thick walled steel disposal casks (0.25 m) surrounded by compacted bentonite. After the re-saturation of the bentonite buffer, the corrosion of the steel disposal casks under anoxic conditions will start. The casks will fail after about 10’000 years of the post disposal, groundwater will reach the HLW and SP, and they will begin to slowly dissolve. Radionuclides (e.g. uranium) will be released into the engineered barrier system and then subsequently into the host rock.

The large quantities of Fe(II) present in the repository near field due to corrosion will influence the in situ repository conditions thus the retardation of radionuclides. It has experimentally been shown that the presence of Fe(II) in the system reduces the uptake of radionuclides due to sorption competition (SOLTERMANN et al., 2013). Additionally, the sorption of Fe at clay minerals can substantially be enhanced by structural Fe(III) due to redox processes (SOLTERMANN et al., 2014). Therefore, the molecular level understanding of the radionuclides binding mechanisms is indispensable to comprehend the competing uptake mechanism of the relevant transition metal ions. It has been demonstrated that the combination of X-ray absorption fine structure (XAFS) spectroscopy techniques and ab initio calculations is a promising tool for the investigation of such complex environmental systems on the atomistic level. The data analysis of XAFS spectra allow in the best cases determining the nature of the surface complexes formed at clay mineral edge sites. Molecular simulations based on density functional theory (DFT) are suitable to ascertain the preferential occupation sites of the clay particles and to serve as the basis for the interpretation of the XAFS data analysis (CHURAKOV & DÄHN, 2012; KÉRI et al., 2017).

In this study, we applied ab initio calculations to interpret the Fe K-edge and U L-edge XAFS measurements on Fe-bearing clay minerals. The theoretical extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectra of structural and adsorbed Fe(III) as well as Fe(II) in clay minerals were obtained on the basis of the ab initio molecular dynamics simulations. The calculated spectra were compared with the experimental measurements. The comparison confirmed that montmorillonite incorporates iron in Fe(III) state. The analyses of the lattice energies of the substituted Fe in montmorillonite suggested that Fe(II) -> Fe(III) redox reaction may occur between the Fe atoms adsorbed on the surface and incorporated structurally into the bulk. The EXAFS and XANES spectra of uranium at the most relevant edge sites of clay minerals were also calculated based on ab initio simulations to get insight the molecular level understanding of uranium binding mechanism.

Acknowledgments

The research leading to these results has received funding from the Swiss National Foundation (SNF) through project number SNF-200021_156412 (2015-2018). The work was supported by grants from the Swiss National Supercomputing Centre (CSCS) under project ID “s620” and “s750”. The use of computer resources of the Merlin 4 Cluster, Paul Scherrer Institute is also gratefully acknowledged. Calculations were performed on UBELIX (http://www.id.unibe.ch/hpc), the HPC cluster at the University of Bern.

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Clay mineralogy of sediments from the Vistula River and the Gdańsk Bay (Poland)

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The aim of the present study was to investigate mineral composition of the clay fraction separated from Vistula River loads and the clay fraction separated from sediments of proximal and distal delta of the Vistula River deposited in Gdańsk Bay.

The river loads (i.e. suspended clays) were collected during high-water stage from several spots located along the Vistula River whereas bottom sediments were collected from proximal delta and from two cores located within the distal part of the delta. Clay fractions from collected samples were separated using Jackson's procedure. The river loads and separated clay fractions (<2 and <0.2 μm) were analyzed using X-Ray diffraction. Position of O-D stretching band was measured using attenuated total reflection infrared spectroscopy and mean layer charge of the samples was calculated (KULIGIEWICZ et al., 2015).

Mineral compositions of the river loads were similar in all studied samples. XRD oriented patterns were dominated by swelling minerals (containing smectite and likely vermiculite), illite, and kaolinite. In 060 region of random XRD patters broad reflections (~1.49 Å) belonging to dioctahedral minerals were observed. The mean layer charge (0.48-0.50 per formula unit (p.f.u.)) was also similar in all samples. Slightly higher layer charge was observed in clay fraction separated from bottom sediments of proximal the Vistula delta (~0.53 p.f.u.). XRD patterns also indicated presence of swelling phases, illite, and kaolinite. A presence of likely hydroxy-interlayering within the swelling phases was indicated by the fact that the 001 reflections were at ~14 Å when analyzed in air-dry conditions. The clay fractions separated from two cores of sediments collected within the Gdańsk Bay showed mean layer charge ~0.48 p.f.u. In the XRD patterns slight increase in intensity of ~10 Å reflections relative to swelling phases 001 reflections down the profile was noticeable. The swelling phases also showed the likely presence of some interlayering.

Obtained results indicated that formation of illite and hydroxy-interlayered clays at the expense of swelling phases are the most likely reactions taking place during early diagenesis of sediments deposited in the Gdańsk Bay.

Acknowledgments

This study was financed by National Science Center Poland (NCN) [grant number: UMO-2016/23/N/ST10/01388].

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Strategies of background treatment in X-ray powder diffraction analysis of clays

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The discrimination between phase specific diffracted intensity and intensity what cannot be assigned to any mineral phase (“background”) is one key issue in X-ray powder diffraction analysis, in general. In clay mineral analysis, diffraction peaks are often extremely broadened, approaching a quasi continuous coherent scattering over the diffraction angle, what is especially hard to separate from any non-specific intensity. The application of inappropriate models for one or both intensity distributions may cause wrongly calculated phase abundances, e.g. by parameter correlation in Rietveld analysis, or by wrong calibration of reference intensities or scale factors in other pattern summation methods. This problem seems to be undervalued in the community, as can be concluded from the sparseness of related papers in the methodical literature.

Notwithstanding that the possible physical contributions to background intensity are well known from theoretical point of view, a general model based on the fundamentals is practically impossible to apply. Instead, rather empirical models without any direct physical relevance like polynomial expressions or even user-defined background definitions are applied in the daily practice. Examples of erroneous approaches and their impact on the results will be demonstrated.

In the author’s opinion, any manual background definition will cause unreproducible results and should not be practiced. Instead, automatic refinement of models with a maximum of physical relevance and a minimum of freely refineable parameters should be applied.

To establish a practicable approach, the first step should be a complete removal of instrumental artefacts causing modulations in the background of a perfectly ordered sample. Typically the divergence, anti-scatter and receiving slits as well as detector settings can be optimized for a simple, maybe linear instrumental background run over the diffraction angle. As sample fluorescence can typically not be completely removed but is proportional to the irradiated sample volume, the use of theta-compensating divergence slits is recommended to get a simple, linear background run from instrument noise and sample fluorescence, together. The sample-to-sample variability of these effects may be typically modelled by a linear function or in maximum by a three-parametric background polynomial. Such easy models are easily to be refined, without significant tendency to be correlated with any phase profile parameters.

However, real clay samples may contain significant amounts of amorphous components, e.g. volcanic glass, opal-A, amorphous iron oxihydroxides, organics or surface adsorbed water. Their scattering function typically forms at least one or more broad "bumps", what could be fitted empirically by polynomial functions with a higher parameter count, maybe in the magnitude of 5 to 10. Such complicated models may cause unpredictable convergence behaviour, maybe towards wrong minima. Warning signals are varying calculated phase contents when the parameter count of the background model is changed. Thus, the number of parameters should be reduced as far as possible. Probably the best solution is a linear fitting of a "reference background pattern", if the amorphous component is known and a reference pattern is available. Such patterns may be also derived from similar samples pattern fitting, or from difference plots of any treated and untreated sample patterns.

In the case that the kind of amorphous component is completely unknown and the background is obviously modulated, but any chemical treatment cannot be performed for practical reasons, all calculated phase abundances should be taken with special care. Especially, the correlation coefficients or derived e.s.d.'s of the phase contents must be evaluated critically. Cross-checking by applying internal standard techniques may help to identify nonsense overestimation of disordered clay mineral phases. But a simultaneous quantification of disordered clay mineral phases and amorphous components remains a challenge.

Acknowledgments

This summary was strongly motivated by the experiences made during the participation in six Reynolds Cup contests. Thanks to the organizers for their efforts to compose challenging reference samples!

Elemental mobilization during burial diagenesis of illite-smectite mixed-layer clays in the Beaufort-Mackenzie Basin, Arctic Canada

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The diagenetic transition of smectite to illite involves the mobilization of numerous elements, but their behaviour has rarely been dealt with due to difficulties in isolation of pure substance from nature. I-S mixed-layer clays (I-S) in the Beaufort-Mackenzie (B-M) Basin, Arctic Canada have been scrutinized on the basis of mineralogical analysis of 215 core and cutting samples from 22 hydrocarbon exploration wells onshore and offshore (KO & HESSE, 1995). The size fraction of less than 0.1 μm consists mainly of I-S, for which geochemical analyses were conducted (KO et al., 1995).

I-S mineralogy and geochemistry display systematic depth trends. The proportion of the I-layers in I-S generally increases with depth, while structural ordering improves from random, a mixture of random and ordered, R1-ordered to R>1-ordered sequence (KO & HESSE, 1995, 1998). As the I-layer content in I-S increases with depth, concentrations of potassium and aluminium increase, whereas that of magnesium decreases. Elemental behaviour is in accord with the reactions of layer-charge development and potassium fixation necessary for the conversion of S-layer into I-layers:
$[(Al_{1.67}R_{0.33})Si_4O_{10}(OH)_2]^{-0.33} + 1.33Al^{3+} \rightarrow [Al_2(Si_3Al)O_{10}(OH)_2]^{-1} + Si^{4+} + 0.33R^{2+}$ and
$[Al_2(Si_3Al)O_{10}(OH2)]^{-1} + K^+ \rightarrow KAl_2(Si_3Al)O_{10}(OH)_2$ where R represents divalent octahedral element. Among trace elements, Rb increases in concentration with depth, and shows a positive correlation with K. Concentrations of Be and V increase with depth and show close correlation each other and with Al, which probably occupied the tetrahedral site because of their relatively small ionic size. Concentrations of octahedral trace elements that may include Co, Cr, Ni, Sc, Zr, and Zr decrease with depth, which would result in reduction in the octahedral layer charge as the release of Mg does. Rare earth elements (REE) show strong positive correlations with Al, Be, and V, and less obvious correlations to interlayer K and Rb, for which they are supposed to substitute because of their large ionic size. The depth trend and covariance of REE with tetrahedral Al, Be and V indicate that I-S diagenesis involves the mobilization of REE. The high valency (+3) of REE could counterpart the local charge imbalance caused by Be^{2+} in tetrahedral sites.

Calculations of structural formulae suggest that the S- and I-layers in I-S appear to have similar structural formulae to natural smectite and illite mineral: $[Al_{1.57}Fe_{0.19}Mg_{0.31}Ti_{0.07}][Si_{3.84}Al_{0.16}]O_{10}(OH)_2$ and $[Al_{1.84}Mg_{0.16}][Si_{3.33}Al_{0.67}]O_{10}(OH)_2$, respectively. The illitization process accompanies a decrease in the octahedral layer charge, while the interlayer ionic charge and the tetrahedral layer charge increase.

Acknowledgments

The study is part of the first author's Ph.D. thesis done at McGill University, Canada in 1992. Travel expenses to attend the MECC 2018 are provided by the Korea Institute of Geoscience and Mineral Resources (KIGAM) through the research project "Smart evaluation solution for oil and gas field based on integration of static and dynamic data (18-3311)".

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Illites and chlorites in hydrothermal alteration of a shallow-dipping epithermal Au-Ag-Pb-Zn-Cu deposit Banská Hodruša, Slovakia

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The intermediate-sulphidation precious and base metal deposit Banská Hodruša at the Rozália mine is hosted by the central zone of a Miocene andesite Štiavnica stratovolcano, located in the Central Slovakia Volcanic Field on the inner side of the Carpathian arc. The gold mineralization is mined 400–650 m below the surface in the Rozália mine, hosted by pre-caldera andesite. The major distinct feature of the deposit is a complex multi-stage vein system with a subhorizontal orientation, which is probably related to an underground cauldron subsidence and exhumation of a subvolcanic granodiorite pluton. Veins are developed on a low-angle normal shear zone, probably corresponding to the base of a sector collapse in the hosting volcano. The unusual structural setting of the deposit resulted in a specific distribution of alteration patterns. Based on the obtained mineral composition of altered rocks, schematically it was possible to define five major types of alteration that occur within the deposit and its vicinity: 1. Silicification with predominant quartz; 2. Strong adularisation with substantial presence of adularia and illite; 3. Weak adularisation with minor presence of adularia and illite accompanied by chlorite and plagioclase, usually affected by albitisation; 4. Strong argillisation with predominance of illite and quartz and with increased concentration of pyrite; 5. Propylitisation equally represented by chlorite, illite, quartz, with plagioclase still present, but without adularia. Alteration patterns occur in a zonal arrangement at the deposit.

Strongest argillisation occurs in the roof of the deposit, forming a continuous horizon above the upper plane of the shear zone. According to XRD analyses, the argillic alteration contains just illite with no smectite neither mixed-layered illite-smectite component. XRD analyses of clay fraction were used for determine illite polytypes and illite crystallinity - the "Kubler index" (KI). KI was used for calculation of crystallisation temperature using the data from the recent volcanic geothermal area in Taupo, New Zealand (JI & BROWNE, 2000). Samples from different parts of the mine showed the presence of $2M_1$ and 1M illite polytypes and variable ratio of both polytypes, but no apparent relationship to a particular vein system was detected yet. KI is also variable, however, illite from the roof of the shear zone always shows similar values (0.49 to 0.52°Δ 2θ). Crystallisation temperature based on KI ranged from 270 to 290°C, which corresponds well to fluid inclusion homogenization temperatures from vein minerals (250 to 310°C). Stable isotope analyses of illite (δD and $\delta^{18}O$) showed isotopically well homogenised fluid of magmatic-meteoric source, where the mixing took place outside of the deposit during the ascent of magmatic fluids from a deep magma chamber. The horizon of argillised rocks in the roof of the shear zone worked as a large-scale collector of vapor and gasses escaping from boiling hydrothermal fluids from the entire thickness of the shear zone, while the extensive fluid boiling during subhorizontal flow of hydrothermal fluids along the shear zone is responsible for precipitation of gold.

Mafic minerals (mostly biotite) are typically replaced by chlorite, however, chloritisation has probably occurred during several stages. Chemically, chlorites belong to the clinochlore – chamosite series, close to the clinochlore end-member. Their Mg/Fe ratio is variable and it does not correlate with the type of veins in their vicinity, neither with the distance to the veins. Interestingly, chlorite in rocks hosting earlier vein systems have increased MnO content (up to 5.4 wt%), which corresponds to the presence of Mn-rich minerals in these veins, including Mn-rich chlorite (up to 10.2 wt% MnO). Chlorite in rocks hosting other vein systems or no vein systems have significantly lower MnO content (up to 2.5 wt% or up to 1.6 wt%, respectively). Temperatures of chlorite formation were estimated using semi-empirical thermometer of BOURDELLE et al. (2013). Vein-filling chlorites always revealed slightly higher formation temperatures (260–320°C) than those of alteration chlorites from hosting rocks (210–300°C). No significant differences were observed for chlorites related to individual mineralization stages.

Acknowledgments
This work was supported by the grants VEGA No. 1/0560/15, APVV-15-0083 and the company Slovenská banská, spol. Ltd.

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Hectorites from the Lyles deposit, Arizona, USA, and Agua Fria, Sonora, Mexico

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Hectorite is an important industrial commodity used in cosmetics, pharmaceuticals, and drilling fluids, and is a potential source of lithium. The formation of hectorite is related to an anomalously Li-, F- and Mg-rich lacustrine environment. Various genetic models for the formation of hectorite have been proposed involving the replacement of volcanic ash or direct precipitation in saline lakes and association with hydrothermal springs (AMES et al., 1958; STARKEY, 1982; CALVO et al., 1999).

Here, new geological, mineralogical, and chemical data of the Lyles hectorite deposit located in the transitional zone between the Basin-and-Range province and the Colorado Plateau and the Agua Fria prospect, Sonora, Mexico, are presented. The Lyles hectorite is interbedded in Miocene to Quaternary lacustrine sediments and tuffs, and composed of an economic upper cream-white and an inaccessible lower green clay bed. A distinct volcanic ash marker horizon can be traced throughout the deposit (NORTON, 1965). The Agua Fria prospect is part of an Oligocene to Miocene volcano-sedimentary basin sequence with clastic sedimentation (GARCÍA et al., 2014).

The microfabrics and mineral compositions were characterized in thin-sections, scanning electron microscopy (SEM), and by X-ray diffraction (XRD), while chemical compositions of bulk samples and clay separates were determined by ICP-MS analyses.

The mineral composition of the clays and marls in both deposits is characterized by authigenic silicates and carbonates. Smectite (27–91 wt%), calcite (6–69 wt%) and dolomite (<1–36 wt%) are the dominant components with minor amounts of zeolites (up to 17.4 wt%). XRD traces of the clay separates reveal trioctahedral smectite (d_{060} at 1.52 Å) with small (<2 wt%) amounts of calcite in Lyles, and small amounts of feldspar, calcite, dolomite and a dioctahedral (illite?) clay mineral (d_{060} at 1.50 Å) in Agua Fria. The SEM images reveal well-preserved, idiomorphic smectite flakes in the groundmass, pore-lining flakes and "sod"-like coatings on zeolites, carbonates and detrital components. Micritic dolomite and sub- to euhedral porous analcime are considerably more abundant at Agua Fria, and occur together with abundant detrital quartz and igneous rock fragments. Strontianite is frequent in the Lyles deposits, while phillipsite, and chalcedony are minor components in both deposits. Relics of volcanic glass shards were generally not observed in the hectorite beds, but are frequently found in the zeolite-rich marker horizon at Lyles and only very rarely as rounded, isolated grains at Agua Fria.

Bulk samples and clay separates have relatively high Li (746–3830 ppm) and Sr (569 to >10000 ppm) but low F (0.21–2.62 wt%) concentrations. Structural formulae indicate F- and Li-poor hectorite with elevated aluminium content in volcanic ash-bearing material at Lyles. The structural formulae suggest a F- and Mg-poorer, Fe-rich saponite-like smectite at Agua Fria. Bulk ∑REE concentrations are low (13–104 ppm Lyles, 80–109 ppm Agua Fria). Material from Lyles completely lacking evidence for volcanic glass or detrital material has low ∑REE (<19 ppm) and Zr (<12 ppm) concentrations. Also in Lyles, higher ∑REE (96–104 ppm) and Zr (up to 173 ppm) concentrations are found solely in samples containing relict volcanic glass, and exceed most corresponding values for samples from Agua Fria that contain detrital igneous rock fragments.

The microfabrics, mineral and chemical compositions suggest concomitant smectite and disseminated carbonate precipitation from highly alkaline, bicarbonate- and fluoride-rich water with high Sr concentrations. The phillipsite and high ∑REE content in the volcanic ash beds of Lyles indicates that zeolite formation was enhanced in horizons bearing volcanic ash. Analcime in the dolomitic mudstones and marls from Agua Fria formed in the groundmass and unrelated to volcanic or igneous material. The abundance of analcime in Agua Fria also suggests more saline and Na-rich conditions.

Detrital material and volcanic ash have a distinct influence on the mineral and chemical composition of authigenic lithium-bearing smectite-rich clays formed in two distinct depositional settings.

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Highly ordered α-zirconium phosphate intercalate with *p*-aminoazobenzene: structure refinement and interaction with UV radiation revealed by molecular modelling

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The layered α-zirconium phosphate (ZrP, $Zr(HPO_4)_2{\cdot}H_2O$) readily undergoes organic modifications and thus new functional materials are formed (MOSBY, 2014). In the presented work a photoactive molecule, *p*-aminoazobenzene (pAz, C_6H_5–N=N–C_6H_5–NH_2), was intercalated into the interlayer space of ZrP. The molecule exhibits *trans-cis* isomerization upon UV irradiation (BANDARA & BURDETTE, 2012), thus the photoresponse of the whole ZrP–pAz complex was expected. In order to understand the processes at the molecular level the structure of the complex was investigated.

The ZrP, synthesized according to SUN et al. (2007), was stirred in a pAz ethanol solution for 24 h at 22°C. The dried and ground product was subjected to the XRD, FTIR and CHN elemental analyses. Structure of the intercalate was determined using real space methods implemented in FOX software (FAVRE-NICOLIN & CERNY, 2002). The obtained model was refined with the JANA2006 program (PETRICEK et al., 2014) using Rietveld method. The sample was irradiated with UV, which was followed by recording the XRD pattern, FTIR and UV–Vis spectra. The results were supported with molecular simulations performed in LAMMPS software using Universal Force Field (UFF).

The intercalate structure was described in monoclinic system (space group *P21/c*) with cell parameters: a=30.184(12) Å, b=5.246(6) Å, c=8.938(4) Å, β=94.62(13)º. The pAz intercalation resulted in the basal spacing increase from 7.6 to 30.0 Å. The ZrP layer geometry was preserved and its thickness was 6.9 Å, thus the remaining interlayer space (23.1 Å) was enough to accommodate two pAz molecules arranged oblique to the ZrP layer. In the FTIR spectra the pAz bands related to the NH_2 vibrations shifted to higher energy, characteristic for the protonated NH_3 group, while the intensity of phosphate OH bands decreased due to their deprotonation. It was concluded that a hydrogen bond was formed between the ZrP layer and the pAz molecule: $Zr–PO^-....NH_3^+$–Az and a stable structure was obtained.

No changes were observed in the XRD pattern nor the FTIR spectra upon UV irradiation of the sample. A slight decrease of the π-π* band in the UV-Vis spectra suggested that a part of pAz molecules could transform to the *cis* isomer. Potential energy calculations for C-N=N-C torsional angle rotation of pAz hydrogen-bonded to the ZrP surface showed no significant differences between energies of *cis*- and *trans*-isomers in comparison to pAz in vacuum or water. However, a preference of *trans* conformation was manifested by a shift of angle with maximum energy of about 10°. Considering the mechanism of isomerization this can explain lack of changes in the XRD patterns after UV irradiation.

Acknowledgements
This study was financed under AGH University of Science and Technology research grant no. 15.11.140.186.

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Evaluation of bentonite deposits from Greece for industrial applications

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Clay minerals find numerous industrial and environmental applications due to their outstanding physical and chemical properties. These applications include environmental protection, remediation, engineering, construction, agriculture, pharmaceutical and various process industries (CHRISTIDIS, 2011). Bentonites, which are important industrial clays rich in smectite, have attracted intense research interest because after processing they allow the development of high added value materials with novel applications in a variety of uses.

Recently, bentonite deposits from the islands of Chios and Samos, eastern Aegean and from areas of Thrace (Skaloma, Sappes), NE Greece have been assessed for their mineralogical and geochemical characteristics and for their potential use in traditional industrial applications. Bentonites from Chios Island consist of smectite, SiO_2-polymorphs (opal-CT or opal-C), dolomite and minor quartz, plagioclase and calcite. Samos bentonites consist of smectite, SiO_2-polymorphs (opal-CT and/or opal-C), quartz and K-feldspar. In Thrace, the bentonites of Skaloma area are characterized by the presence of smectite, SiO_2-polymorphs (opal-CT and opal-C), calcite and traces of zeolites, quartz and illite. In the area of Sappes the bentonites consist of smectite, quartz, calcite, plagioclase, illite and kaolinite. These low-moderate grade bentonites were classified according to the layer charge of the smectites present, following the characterization scheme of CHRISTIDIS et al. (2006). The smectites in Chios and Samos bentonites are medium-high charge montmorillonites whereas their Thracian counterparts contain low charge montmorillonites (Skaloma) and Fe-rich beidellites (Sappes) (KOUTSOPOULOU et al., 2016).

The CEC of the bentonites varies between 70 and 90 cmol/kg, and is considerably lower in the bentonites from Sappes (40-50 cmol/kg). The bentonites have a moderate swelling index and only in some samples from Chios and Skaloma may be considered as acceptable (above 30 ml gel/2 g clay). The beidellites from Sappes display very low swelling indices in accordance with the smectite content and the crystal chemical characteristics of the smectites. The colour data show that the bentonites from Chios and Samos Islands and Skaloma area (Thrace), have superior colour compared to the Sappes bentonites. Although the presence of silica phases (eg. opal-CT) in the former areas may affect colour to some degree, the presence of Fe-rich beidellite and illite in Sappes and the low smectite content could be the main reason for the poorer colour quality. The specific surface area of the samples ranges between 9 to 38 m^2/g in most samples and can be further increased after acid activation. Indeed, preliminary tests showed that the studied bentonites are suitable for crude oil clarification after acid activation and treatment of the bentonites with different amines has produced a series of organophilic end products, which have been employed in the formulation of clay polymer nanocomposites. The results of the present study show that these moderate-low grade bentonites could be used in high added-value applications after processing.

Acknowledgements
E.K. thanks the State Scholarships Foundation (IKY) for the financial support through the "Reinforcement of Postdoctoral Researchers" (MIS 5001552) programme, OP "Human Resources Development, Education and Lifelong Learning", co-funded by the ESF and the Greek Public Sector.

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Mineralogical and geochemical characterization of Quaternary lacustrine sediments in Rečica clay deposit (Croatia)

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Remnant lacustrine sediments are preserved in the Karlovac depression, Crna Mlaka basin, in the central part of Croatia. This area represents the margin of the Adriatic Carbonate Platform. The Rečica clay deposits developed as Quaternary deposits in Crna Mlaka basin, the River Kupa Valley. Crna Mlaka basin is filled with Quaternary lacustrine/wetland sediments. Its edges are bordered and surrounded by Neogene (Pliocene) lacustrine sediments. Three types of lacustrine deposits are present. Regularly layered and gently inclined, fine-grained sediments (clay and silt) are spatially dominant. The second type is composed of coarse gravels and sands and the third one is composed of colluvial material. Fine-grained argillaceous sediments, generally referred to Pleistocene age, form Rečica clay deposit. The major part of the clays in Rečica clay deposit is represented by grey and yellow clays, brown clays and they are underlain by greenish-grey and grey-blue clays. The clay deposits are 8-12 m thick and overlay karstified limestone bedrock. A total of 171 samples were taken from 36 boreholes covering the entire area of the deposit. These samples, representing 1 to 3 m depth intervals, were used for determining mechanical properties of the material. Complete analyses, including mineralogical and geochemical analyses, were done on 12 composite samples. Clay minerals are dominated by smectite and illite, while chlorite and kaolinite are present in minor amounts. They are associated with quartz and in minor amount feldspar, occasionally goethite. Calcite is absent in lacustrine clays, indicating predominance of siliciclastic river supply. Abundance of smectite decreases in the surface sediments. SiO_2 and Al_2O_3 dominate the clay geochemistry among other oxides. Geochemical and mineralogical analyses of the fine-grained varieties of lacustrine clays showed that their composition primarily depends on geology of the catchment area and secondarily on environment of deposition. The material was probably supplied by river. A montmorillonite-illite association is expected in closed lakes. Discovery of lake system bears on idea of river network in the Early Quaternary. These landform sequences provide an archive of long term fluvial and lake landscape development. The existence of the lakes in Crna Mlaka continental basin can be related to the period of the Pliocene-Pleistocene-Holocene. The basin is mainly characterized by fluvio-lacustrine sedimentation.

Structural iron release from bentonite by Y^{3+} and La^{3+} ions

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Our previous study (KOVÁCS et al., 2017) of La ion exchange of Ca-bentonite has shown extreme values of sorption of La ions (higher than cation exchange capacity), while iron content of La-bentonite has decreased compared to that of Ca-bentonite. Our conclusion has been that lanthanum ions can somehow supersede iron from the octahedral positions of crystal lattice. We assume that the departure of positively charged iron ions from the lattice increases the negative layer charge and the cation exchange capacity. This motivates our studies of enhanced sorption of lanthanum and yttrium cations.

To prove our previous statement, in this work the main question was the change of the composition in the Ca-bentonite depending on the pH, and concentration during the Ca-H, Ca-Y and Ca-La cation exchange procedure. X-ray fluorescence analysis was used to follow changes in the chemical composition (mainly the concentration of Y^{3+}, La^{3+}, Ca^{2+}, Fe^{3+} ions) in the solid phase.

Firstly, the results revealed that pH has a high influence during the Ca-H cation exchange procedure. The more acidic solution the more calcium was exchanged. In this case, iron loss was not observed.

On the other hand, the results show the extent of the exchange between the divalent calcium ion and the trivalent yttrium and lanthanum ion, depending on the pH and concentration, and also the change of the structural iron(III) of the bentonite. The XRF results prove that the pH (in the pH range of 3.5–5.5) slightly influences the exchange between Ca, Y and La ions. The different concentrations influence the structural iron content of bentonite in the case of the exchange of calcium ions to trivalent yttrium and lanthanum ions. In the case of trivalent ion exchanged bentonite the greater concentration the more iron was released.

Thus, the pH has low influence, meanwhile the concentration has higher influence to high amount of iron loss during divalent- trivalent cation exchange. These results strongly confirm our previous study.

Acknowledgments

This study was financed by the EU and co-financed by the European Regional Development [GINOP-2.3.2-15-2016-00008]; the Hungarian National Research, Development, and Innovation Office [NKFIH K 120265].

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Red soils in Mugla polje, SW Turkey: Mineralogical and Geochemical Approach

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Red Mediterranean Soils (RMSs) are basically defined as the red colored soils developed under Mediterranean climatic conditions. They are observed as infills on the hard limestone and dolomite; and as discontinous layers on any type of hard bedrock as well as on unconsolidated sediments (FEDEROFF & COURTY, 2013). Terra Rossa term, on the other hand, is used to define a reddish clayey to silty-clayey soil which covers limestone and dolomite in the form of discrete layers as well as in the form of infilling of karstified cracks (DURN et al., 1999; DURN, 2003). Mugla polje (SW Turkey), which is bounded dominantly by Liassic carbonate rocks and Miocene clastics, is a typical karstic depression. Red colored soils developed as infillings on hard limestone and dolomite and reddish-brownish colored soils as top soils on unconsolidated alluvial and colluvial sediments from Mugla polje are the main subjects of this study.

Major aim is to investigate the soils developed over different parent materials in terms of mineralogical, and geochemical properties. For this purpose, red soils found within the fractures of hard calcareous bedrocks are called Terra Rossa; while the ones developed rather as red strata on unconsolidated parent materials in the lowlands of the polje are called Red Mediterranean Soils.

Sampling was performed on 4 Terra Rossa soils and 8 Red Mediterranean Soils (6 over alluvial sediments; 2 over colluvial sediments). The grain size distribution of the soil samples was measured using soil hydrometer 152H based on ASTM D7928 standard test method. Dry soil colours were determined using Munsell colour charts. Cation exchange capacity (CEC) of each sample was measured by methylene blue test according to the methods of JONES (1964). Soil samples were analysed mineralogically by Panalytical Expert Pro diffractometer equipped with a Cu tube at 40kV voltage and 30mA current with a scanning rate of 2º/min. Whole rock chemical analysis of the major elements was performed by Thermo ARL X-ray fluorescence on powder pellets. Molecular weathering ratios were calculated based on the major oxide compositions to reveal the calcification, salinization, clayeyness and base loss according to the equations given in RETALLACK (1997; 2001) and SHELDON & TABOR (2009). Chemical index of alteration (CIA) was calculated by using the molecular proportions (NESBITT & YOUNG, 1982). Thin sections were prepared to describe mineralogical and petrographical properties of the parent rocks. Morphology and elemental concentrations of the grains were examined using QUANTA INSPECT F50 and EDAX OCTANE scanning electron microscopy with an accelerated voltage set to 20 kV.

Terra Rossa soils are found to be clay; while RMSs are clay, clayey to silty and sandy loam according to the particle size distributions. Both types of soils have minerals with low CEC values. Bulk mineral composition for both soil types are composed of calcite, quartz, feldspar, clay minerals and small amount of dolomite. However, only Terra Rossa soils include pedogenic hematite. Dominantly kaolinite and associated illite, chlorite and chlorite-vermiculite mixed layer (?) minerals form the clay fraction of both soil types. Terra Rossa soils show the molecular weathering ratios of normal salinity and calcification; while strong clayeyness and moderate base loss. On the other hand, those of RMSs indicate normal salinity, normal clayeyness, normal to moderate base loss and moderate calcification intensities. Chemical index of alteration (CIA) values are very high (78-88 %) for Terra Rossa soils; while low (10-20 %) for RMSs.

Acknowledgments
This study was financially supported by The Scientific and Technological Research Council of Turkey (TUBITAK) with 116Y027 project.

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Kinetics of rehydroxylation in dioctahedral 2:1 clay minerals: reaction mechanisms and implications for archeometric dating

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Clay minerals lose structural OH groups when heated in a process of dehydroxylation. In dioctahedral 2:1 sheet silicates dehydroxylation occurs in temperatures between 300 and 800°C and is reversible under certain circumstances (DERKOWSKI & KULIGIEWICZ, 2016). The process of regaining structural OH groups in a dehydroxylated phase (rehydroxylation) results in mass gain. Rehydroxylation of a fired clay material takes place in Earth's surface conditions and is the foundation of a newly proposed archeometric dating technique of ceramic artefacts, called rehydroxylation dating (RHX dating; WILSON et al., 2009). However, the mechanism and kinetics of rehydroxylation are not well-understood, making the crystallochemical principles standing behind RHX dating still missing. In the present study, an attempt was made to provide a detailed kinetic description for dioctahedral smectites saturated with different interlayer cations, as a model for reactions potentially occurring in ceramic materials.

Two reference smectite samples: SWy-3 (*cis*-vacant) and SCa-3 (*trans*-vacant) obtained from the Source Clay Repository of the Clay Minerals Society in Cs^+, Ca^{2+}, and Mg^{2+} forms were used. A series of a thermogravimetric (TG) experiments was performed in order to quantify rehydroxylation *in-situ* (Fig. 1). The obtained data were used to estimate the potential of rehydroxylation as a function of temperature of prior dehydroxylation and the interlayer cation type. Model-fitting methods of activation energy (E_a) calculation were applied to mass-gain data in order to determine reaction mechanism and the values of E_a of rehydroxylation.

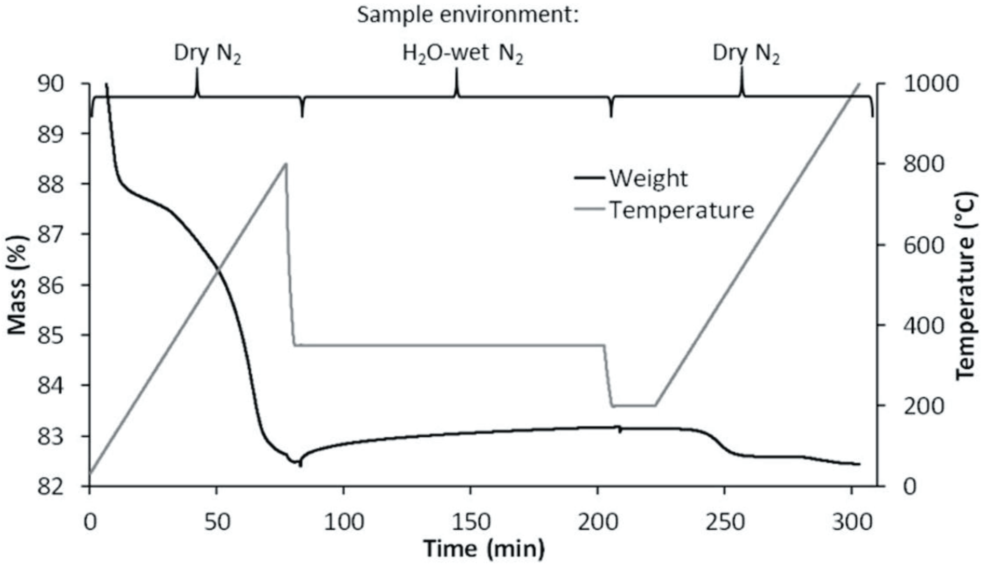

Figure 1. An outline of TG experiment, involving three phases: 1) primary dehydroxylation under dry nitrogen, 2) in situ rehydoxylation under H_2O-saturated gas flow, and 3) secondary dehydroxylation under dry nitrogen.

Cs- and Mg-exchanged forms of smectites presented higher potential for rehydroxylation than corresponding Ca-exchanged smectites. Cs and Mg facilitate rehydroxylation by different mechanisms: the presence of Cs^+ in the interlayer increases d-spacing of a dehydroxylated smectite due to its large cationic radius. Mg^{2+}, in turn, locally neutralizes octahedral charge during primary dehydroxylation due to the Hoffmann-Klemen effect, which introduces layer charge heterogeneity that - in combination with high affinity of H_2O molecules for Mg^{2+} cations (high hydration enthalpy) - facilitates rehydroxylation. The decrease of the temperature of dehydroxylation increased the rehydroxylation potential in both studied smectites, irrespectively of the interlayer cation type.

Kinetic analysis showed that rehydroxylation follows the two dimensional diffusion and is a rate-limiting process. The rehydroxylation kinetics were found to differ in high (>300°C) and low (<300°C) temperature conditions, which means that E_a values obtained for high-temperature rehydroxylation experiments might not be applicable in RHX dating procedures involving low-temperature rehydroxylation measurements.

Acknowledgments
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Applying a thermogravimetric quantitative method for the determination of dehydroxylation and dehydrogenation in Fe-chlorites

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A thermogravimetric quantitative method is commonly used to determine the content of H_2O in phyllosilicates, both the adsorbed species, and the molecules produced by OH groups in the course of dehydroxylation ($(OH)_{2n} \rightarrow nH_2O + nO_r$). However, such a quantitative assessment matches theoretical calculations only in the case when the dehydroxylation is the sole process during the heating. Thermal decomposition of Fe(II)-containing phyllosilicates, however, involves also dehydrogenation, which removes hydrogen atoms and oxidizes structural Fe(II) [$2nFe^{2+}\text{-}OH \rightarrow 2nFe^{3+}O + nH_2$]. The loss of hydrogen from OH groups results in less OH available to dehydroxylation, decreasing the total mass losses as determined by thermogravimetry.

In order to check the validity of thermogravimetric (TG) methods to distinguish the two reactions, seven monomineralic, tri-,trioctahedral chlorites from a common Mg-Fe series were selected for the study. Mass losses evolution was tracked under ramp heating conditions up to 1000°C with 5, 10 and 20°C/min rates, in pure nitrogen flow, in which dehydrogenation produces H_2 whereas dehydroxylation produces H_2O. In order to enhance dehydrogenation, isothermal heating experiments (350-475°C for 24 and 48 h) on a selected chamosite were performed. Because the mass loss is dominated by dehydroxylation (9 x greater than mass loss from dehydrogenation) TG experiments were coupled with a quadrupole mass spectrometer in order to track a relative ration of H_2O and H_2 in evolved gases. Selected samples were analyzed with Mössbauer spectroscopy to observe a progress of oxidative dehydrogenation. To ensure an oxygen-free environment, CuC_2O_4 was analyzed periodically in the TG furnace purged under the above-mentioned conditions.

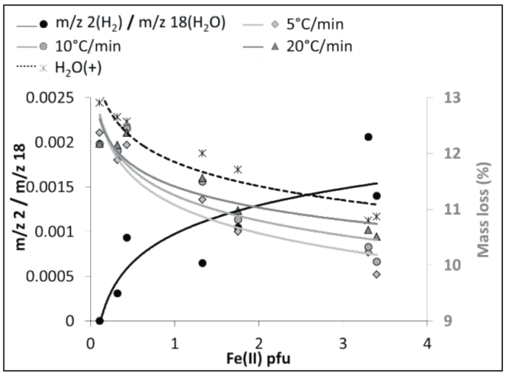

Figure 1. The relationship between the total ratio of H_2/H_2O evolved during 20°C/min heating rates and the experimental total mass losses obtained under 5, 10 and 20°C/min ramp heating rates in nitrogen gas atmosphere, plotted as a function of Fe(II) content in the studied tri-,trioctahedral chlorites.

All experimental mass losses for Fe(II)-containing chlorites were lower than the theoretical mass losses calculated from mineral formula using the pure dehydroxylation reaction ($H_2O(+)$; Fig. 1). The deviation from $H_2O(+)$ increased with Fe(II) content in a chlorite structure and inversely correlated with the total H_2/H_2O ratio released from the samples during the ramp heating. A particular heating protocol affects the TG results: the lower the ramp heating rates, the lower the experimental mass losses. Moreover, the strongest reduction in total mass losses, up to 28 % relative, was obtained when ramp heating procedure involved a prior isothermal heating step. The dehydrogenation occurring under inert gas atmosphere excludes the possibility of accurate determination of OH content for all Fe(II)-bearing phyllosilicates (ROUXHET et al., 1972). In chlorites, such a determination requires TG data aided by measuring the extent of Fe(II) oxidation by an ex-situ method (e.g., Mössbauer spectroscopy) in order to estimate how much H was consumed by dehydrogenation thus now available for dehydroxylation.

Acknowledgments
This study was funded by the National Science Centre, Poland under research project no. 2017/27/N/ST10/02544.

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Mineralogical and geochemical study of the marine sediments of south Aegean Sea: implications for provenance

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Sediments from three deep-sea bottom gravity cores in the Myrtoon Basin SW Aegean (KIM4), Creta Sea South Aegean (TI13) and SE Aegean Sea (ST5), Greece, were examined by quantitative mineralogical and geochemical analysis in order to discuss the factors controlling its geochemistry and obtain data that might be used as destination and transport tracers for futher information on the provenance of the sediments. The studied sediments consist mainly of muds rich in carbonates and in certain levels, which vary in the different cores, they contain material rich in organic carbon that corresponds to the recent sapropel S1. The main minerals in the sediments are carbonates (calcite, Mg-calcite, aragonite, dolomite), quartz, feldspars and clay minerals (illite, chlorite, kaolinite, smectite and palygorskite). The clay mineral assemblage is characterized by increased illite content, chlorite, and lesser kaolinite and smectite. The sapropelic sediments are characterized by a sharp decrease of the Mg-calcite content.

The mineralogical approach included quantitative analysis of the bulk sediment samples by Rietveld refinement with the BGMN code (Autoquan software). In addition the abundances of smectite, illite, chlorite and kaolinite were determined according to (BISCAYE, 1964), and were compared to the clay mineral abundances in the bulk samples. This comparison revealed that smectite is enriched in clay fraction while chlorite and kaolinite are enriched in the bulk sediment. The highest illite contents are observed in the KIM4 core in the Myrtoon Basin decreasing eastwards. Core ST5 from the SE Aegean contains minor hornblende and serpentine suggesting influence from an ultra-basic component, whereas core TI13 contains glass shards that suggest volcanic contribution from Santorini Milos and possibly Nisyros volcanic islands. Illite and chlorite originate from the metamorphic and sedimentary basement rocks which are present in the nearby land masses of Turkey, the SE Balkan Peninsula and the Aegean Islands.

All sediments are composed of a mixture of biogenic carbonate minerals (main sources of Ca and Sr) and silicates, mainly quartz. The sapropelic horizons show high concentrations of terrigenous elements and low concentrations of carbonates. The highest abundance of carbonates is observed in the W. Aegean Sea (Myrtoon Basin) whereas the abundances of the aluminosilicates follow the opposite trend. Strontium, Ba and U are also enriched in the sediments of Myrtoon basin compared to the remaining study areas. In the sapropelic horizons the increase in organic carbon is accompanied by similar increases in Ba content. The upper youngest sections in the sediment sections is characterized by increased productivity. The organic carbon contents of the bottom sediments from Aegean Sea are enhanced and varied between 0.3 % and 2.2 % with a tendency for higher values in the silt sized fraction.

The sediments in the Southern Aegean Sea (Cretan Basin) have received volcanic input related to the South Aegean Volcanic Arc namely the volcanoes of Milos to the west Santorini in the centre and Nisyros to the east. The presence of kaolinite is related to multiple sources, with ~50 % being related to aeolian input. Palygorslite is also attributed to aeolian origin. The age model based on radiocarbon dating showed highest sedimentation in the SE Aegean Sea and lowest in the Cretan Basin, in accordance with the influence of the terrestrial input from the nearby Turkish landmass and the circulation patterns in the Aegean.

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Clay mineralogy of the soils from high belt of the Altai Mountains

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The extensive areas in the highlands located at the junction of the Altai and the Sayan Mountains are to be regarded as the mosaic distribution and interaction of tundra and steppe vegetation formed in the dry and cold environments (AMOSOV, 2016). The soils of these landscapes have been inadequately studied due to inaccessibility of the areas. One of such areas affected by glaciation was located in the lake basin of the Dzhulukul, in the plateau of Chulyshman at a height 2200 m in the Altai Mountains. The soils here are very close to those in the cold environments of tundra zone despite the pronounced "steppe" features, and occupy the ecological niche between soils of humid tundra and cryoarid steppe zones. In the study plot the dominant soils of the flat areas with cryogenic micro-relief and dwarf birch - gramineous tundra vegetation with spots of moss and lichens are represented by Turbic Cryosols. These permafrost-affected soils are loamy, acidic – neutral with gleyey spots and pronounced humus ("soddy") horizon, which is not common for the tundra soils, with high content of soil organic matter. On the sandy and gravelly-sandy hills with lichen - gramineous vegetation with motley grass and sagebrush the well-drained, permafrost-free, and acidic Entic Podzols with dark humus films on pebbles due to Al-Fe-humic migrations have been formed (LESSOVAIA & GORYACHKIN, 2007).

The aim of the present research was to investigate the response of clay minerals to modern pedogenesis based on the soil profile data. The <1 μm fraction obtained by soil sedimentation and decantation in a water column was studied using X-ray diffraction measurements of textured specimens.

Di- and trioctahedral micas and chlorite dominate in the fine size fraction of Turbic Cryosols; besides kaolinite and admixture of quartz were identified. Modern pedogenesis led to: (i) appearance of low content of irregular mixed-layer mica-smectite (vermiculite) due to mica transformation and (ii) decrease of chlorite content in the acidic soil horizons above the bottom (BC) one underlain by permafrost. In the upper horizons the overall reduction of clay mineral intensities in the XRD patterns of textured specimens was observed. Generally the phyllosilicates' redistribution and transformation in the profiles affected by pedogenesis are not pronounced and similar to that in the environments characterized by the extremely weak intensity of chemical weathering such as Cryosols from Yedoma deposits of the Kolyma Lowland (North-East Siberia) or Central Yakutia Plain. For example, the transformation of illite and chlorite to randomly interstratified structures has been documented for Cryosols of Yedoma deposits (ALEKSEEV et al., 2003). In the Cryosols of Central Yakutia, in which fine size fraction high smectitic clay dominates, relative reduction in the contents of both illite and chlorite has been found in the more acidic upper horizons. Illite has been partially transformed to a mixed-layer illite-vermiculite (smectite), whereas chlorite either has been completely decomposed or has transformed to a mixed-layer expandable structure (LESSOVAIA et al., 2013). In lake basin of the Dzhulukul the permafrost-free Entic Podzols are characterized by the same mineral composition as the Turbic Cryosols studied in this area but a more pronounced decrease of chlorite content towards the upper part of the profile was revealed in Entic Podzols.

The findings based on the Cryosols and permafrost-free Entic Podzols illustrated that the clay mineral transformations affected by pedogenesis reflect the weak development of chemical weathering. The latter can be explained by the dry and cold conditions led to formation of steppe elements in the tundra zone.

Acknowledgments

This study was financed by RFBR (grant 18-05-00860a).

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Textural characteristics of rehydroxylated kaolinites

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This paper is focused on the textural characterization of rehydroxylated kaolinites, which are interesting materials as selective sorbents for different contaminants, which requires very efficient removal from aqueous system. Arsenic (As), antimony (Sb) and selenium (Se) are among the toxic elements occurring in small quantities in the water and in the earth's crust. The degree of toxicity of these elements depends on the oxidation degree and the form of occurrence. The effect of As, Sb, Se and their compounds causes both acute and chronic poisoning, often leading to death. The use of kaolinite and rehydroxylated kaolinite as the sorbents of these contaminants belongs to very efficient methods. Under the hydrothermal treatment, kaolinite is transformed into semicrystalline very reactive metakaolinite, and the rehydroxylation of metakaolinite to kaolinite is possible. ROCHA & KLINOWSKI (1991) studied the rehydration of metakaolinite to kaolinite which was heated at 155-250°C for 1-14 days and concluded that the amorphous metakaolinite can be transformed to crystalline form. The specific surface area highly increased during the rehydroxylation. LHOTKA et al. (2012) studied the rehydroxylation of metakaolinite to kaolinite which was heated at 150-250°C for 1-14 days. He found that the rehydroxylation of metakaolinite to kaolinite was strongly dependent on the temperature and time of the hydrothermal process.

The crystalline kaolinite from West Bohemia was used for the preparation of selective sorbents. This kaolinite was calcined at 650°C for 3 h and converted to metakaolinite. For the preparation of rehydroxylated kaolinite, 8 g of metakaolinite was mixed with 30 g of water. The suspension was stirred for 2 min at room temperature and then was inserted into autoclave. The autoclave was heated at 150°C -250 °C for 4, 7, 10 and 14 days. After removal from autoclave, the suspension was filtered off, washed with distilled water and dried at 100°C for 24 h. The samples of rehydroxylated kaolinites were characterized using adsorption of nitrogen. The adsorption isotherms were fitted according the Brunauer-Emmett-Teller (S_{BET}) method and t-plot method ($S_{t\text{-}plot}$) for specific surface area, the micropore volume by the t-plot method and the pore-size distribution by the Barrett-Joyner-Halenda (BJH) method and Density Functional Theory (DFT) method. The specific surface area (S_{BET} and $S_{t\text{-}plot}$), micropore analysis and distributions of volume mezopores were measured on an ASAP 2020 and 3Flex surface analysers (Micromeritics, Norcross, GA, USA) using the gas sorption technique (N_2 at 77 K).

All samples of rehydroxyled kaolines show adsorption isotherms of type IVa (IUPAC classification), so RK samples consist of mesopores with classical type hysteresis loop H3 (IUPAC classification), which corresponds non-rigid aggregates of plate-like particles clays. The samples of rehydroxylated kaolinites were prepared under different reaction conditions. The surface area of the newly prepared kaolinites was much larger than raw kaolinite and metakaolinite (from 15.8 to ~103.1 $m^2\ g^{-1}$). It was observed that the median pore size of the rehydroxylated samples was similar (diameter of pore 6.0 nm). The volume of these pores increased with reaction time of rehydroxylation at the temperatures of 150 and 175ºC. The porous structures of new kaolinites were not fully developed at a rehydroxylation temperature of 150ºC. In the kaolinites prepared at 175ºC, the volume of pores with diameter 6.0 nm was at a maximum, while in the samples prepared at 200 and 250ºC the volume of pores with the same diameter was lower. Between the first and seventh days of rehydroxylation we recorded a decrease in the volume of pores with a diameter of 6.0 nm at the rehydroxylation temperatures of 200 and 250ºC.

The rehydroxylation of metakaolinite to kaolinite strongly depends on the temperature and time of hydrothermal process. The optimum transformation from the point of view of the surface properties was observed after longer-term autoclaving (4-7 days) at 175°C, when the specific surface area - S_{BET} - of raw kaolinite increased more than three times.

Acknowledgments
This work was realized within the Operational Programme Prague – Competitiveness (CZ.2.16/3.1.00/24501) and “National Program of Sustainability“ (NPU I LO1613) MSMT-43760/2015.

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Impact of polymer-characteristics on the hydro-mechanical properties of polycationic modified bentonite

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Challenges arising from increasing global population, i.e. narrowing resources like water and soil, the increasing need for habitat and the densification of urban areas, require the optimisation of several established methods and construction processes in geotechnical and geoenvironmental engineering. The addition of polymers to manipulate the clay water interaction and clay structure is promising to achieve, in several cases, such objectives. Successful applications e.g. modified clay-barriers in order to improve the resistance against destructive environmental impacts (DI EMIDIO et. al., 2017), aggregate stabiliser for agricultural applications (BEN-HUR & KEREN, 1997) and modification of soil properties (i.e. plasticity, permeability and shear strength) in mechanised tunnelling (ZUMSTEG et. al., 2013), to name a few. Although, the efficiency of this technology has been demonstrated successfully in various laboratory studies and practical applications, there is still a lack of understanding regarding the multi-scale behaviour of polymer-enhanced clay. To further improve the efficiency of this technology, a deeper understanding of clay-polymer interaction processes is essential. Polymers are long-chained macromolecules composed of several repeating units, namely monomers, which can be categorised regarding charge (positive, negative, neutral, polar/non-polar), structure (branched/ unbranched), and molecular weight, which equate to the size of the particular polymer chains for a given polymer. The functional groups of the polymer can interact with clay basal planes and edges, exchangeable cations and water molecules. The thermo-dynamical behaviour of polymers in solutions and the interaction with charged and uncharged solids is highly depending on polymer characteristics, nature of the solids, and quality of the solvent (FLEER, 1988). When constrains during mixing permit particular chains to attach itself to more than one clay particle, an additional polymer-bridging takes place (LAGALY et. al., 1997). On the macroscopic scale, effects that arise from modified physico-chemical behaviour and bridging effects are superimposing.

In the framework of the present research, a systematic study on polymer-modified bentonite was conducted with special emphasis on effects of polymer characteristics. Different clay–polymer mixtures were obtained using solution intercalation by mixing bentonite (MX80) and cationic copolymers (polyacrylamide), varying the molecular weight of the polymer. The macroscopic behaviour was studied by means of hydro-mechanical testing (compression tests and hydraulic permeability), determination of engineering index properties (plasticity) and soil water retention behaviour (unconfined shrinkage). Subsequently the impact of reconstitution (drying and grinding) after solution intercalation was analysed. Theoretical approaches relying on the thermodynamical behaviour of polymers in solution were used to identify the impact of polymer-characteristics and boundary conditions on the polymer-clay interaction. The outcome of this study indicates that a more selective use of polymers can increase the effectiveness of polymer-enhancement in technical applications.

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Order-disorder in Mg-Fe chlorites with semi-random stacking based on powder X-ray diffraction data

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Chlorites consist of alternatively arranged, negatively charged 2:1 layers – $(R^{2+}, R^{3+})_3(Si_{4-x}Al_x)O_{10}(OH)_2$ and positively charged interlayer octahedral sheets – $(R^{2+}, R^{3+})(OH)_6$ where R^{2+} commonly equates to Mg and Fe and R^{3+} to Al, Fe, and rarely Cr and Mn. According to the classification proposed by Bailey and Brown (BAILEY & BROWN, 1962) four different arrangements of the interlayer sheet and the 2:1 layer are possible (Ia, IIa, Ib, IIb). In semi-random stacking, adjacent chlorite packages (interlayer and 2:1 layer) are shifted one to each other by additional ±1/3b vector. In such a case, the diffraction *hkl* reflections with k=3n are sharp, whereas those with k≠3n are broad and difficult to ascribe.

These broadened peaks, however, can offer valuable information about the stacking sequences in chlorites. Therefore, the main goal of the present study was to obtain comprehensive understanding about stacking sequences in chlorites as well as the possible admixture of different polytypes, based only on their powder diffraction patterns.

To address this issue, simulations of the diffraction patterns were performed in the Sybilla 3D program developed at Chevron ETC. Modifications of the program code were introduced in the form of additional parameters describing the contribution of ±1/3b shifts ($W_{IIb,y=\pm1/3b}$), the distribution of Fe between the 2:1 layer and interlayer (R_{int}), the percent of layers shifted only in one direction of ±1/3b (R_{shift}), and the percent of different polytypes (W_{Iaa}, W_{Iab}, W_{Ibb}, W_{IIaa}, $W_{IIab,}$ W_{IIbb}) in the structure. Possible mixed-layering of stacking sequences were assumed for only R0 ordering.

Seven pure (<3 % impurities) tri-trioctahedral chlorites with a composition covering the common Mg-Fe (clinochlore-chamosite) series were studied. In all cases, based on *h0l* reflections, the assembly of the 2:1 to interlayer was established as dominantly IIb polytype with the monoclinic shaped unit cells. None of studied chlorites had interstratifications with 7Å mineral.

Based on the simulations, in almost all studied samples the interstratification of different polytypes occurs. The range of admixtures was found from 5 up to 19 %, with no correlation with structural Fe content. Our results agree with data obtained using high resolution transmission electron microscopy by KOGURE & BANFIELD (1998) and INOUE & KOGURE (2016) who showed the presence of several chlorite polytypic sequence including IIab, Iab, Ibb, Iaa. In our fits the IIaa sub-phase was also found.

A detailed description of semi-random stacking sequences shows that the percent of layers shifted by ±1/3b ($W_{IIb,y=\pm1/3b}$) is significant but it is not a sufficient parameter to describe the stacking structure in chlorites. In three samples, where the *hkl* reflections with k≠3n were sharper, the additional parameter of R_{shift} needed to be taken into account, suggesting partial ordering along the [010] direction.

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Near-IR spectroscopy in organoclays study

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This work introduces the major benefits of near-infrared (NIR) spectroscopy in organoclays research. The identification of specific bonds “not visible” in the mid-infrared (MIR) region, characterization of acid-treated organo-montmorillonites (O-Mt), pyridine adsorption on acid-treated Mt, and the conformation of organic cations in montmorillonite interlayers are discussed.

Selected O-Mt, perspective fillers in clay polymer nanocomposites, were prepared from Na-Mt and organic cations containing octylammonium chain(s), hexadecylammonium chain(s) or a benzene ring with or without a reactive double bond. Based on the stretching (ν) and bending (δ) vibrations observed in the MIR region, the first overtone (2νXH) and combination ($\nu+\delta$)XH modes of XH groups (X=O,C,N) were identified. The changes in the intensity of the ($\nu+\delta$)H_2O band allowed the comparison of the amount of water adsorbed on Mt surface. The NIR spectra were extremely useful in identification of NH_2^+, NH^+ and $H_2C=C$ groups, which were difficult to recognize in the MIR region of O-Mt due to overlapping with other absorption bands (MADEJOVÁ et al., 2011).

The effect of the surfactant size on the extent of Mt dissolution in HCl was confirmed for O-Mt prepared from Na-Mt and tetraalkylammonium salts of alkyl-chains length increasing from methyl-Me_4N to pentyl-Pe_4N. A new band near 7315 cm^{-1} due to SiOH overtone revealed creation of reaction product, protonated silica phase. The less stable were Na- and Me_4N-Mt, Et_4N- and Pr_4N-Mt were slightly more resistant mainly at short reaction times. Bu_4N-Mt and Pe_4N-Mt showed the least structural modifications within 8 hours treatments. Bulky alkylammonium cations, covering the inner and outer surfaces of montmorillonite, prevent effectively the access of protons to the layers protecting thus the mineral from degradation in the acid (MADEJOVÁ et al., 2012).

NIR spectra of pyridine adsorbed on untreated and acid-treated montmorillonite were analyzed with intension to distinguish different pyridine species adsorbed on montmorillonite surface. The effect of the mineral structure modification on the formation of acid sites was discussed together with the strength of the pyridine bonding on montmorillonite surface. After exposure of Mt to pyridine vapours the intensity of the ($\nu+\delta$)H_2O band diminished indicating the partial replacement of water molecules by pyridine. The CH overtone band corresponding to physisorbed and/or H-bonded pyridine appeared near 6000 cm^{-1}. Disappearance of the SiOH band in the NIR spectra of acid-treated samples revealed that silanol groups as weak Brőnsted acid sites formed H-bonds with pyridine-nitrogen (MADEJOVÁ et al., 2015).

The understanding the arrangement/conformation of organic cations (surfactants) is an important step toward optimizing the performance of O-Mt in their applications where selective surface interactions are crucial. Detailed information on the local conformation of surfactants provides IR spectroscopy. The positions of the bands related to the vibrations of the CH_2 groups were used as an indicator of the disordered *gauche/*ordered *trans* conformer ratio. Shift of the bands to lower wavenumbers confirmed the increase of *trans* conformers. The comparison of the MIR and NIR spectra of montmorillonite saturated with trimethyl-alkylammonium cations with varying alkyl chain length (even numbers of carbon atoms from C6-C18) showed significantly higher downward shift of CH_2 bands in the NIR than in MIR spectra favouring the utilization of the NIR region for examining the conformation issue (MADEJOVÁ et al., 2016).

Acknowledgments
The financial support of the Slovak Grant Agency VEGA (grant 2/0141/17) and the Slovak Research and Development Agency (grants APVV-15-0741 and APVV-15-0347) is acknowledged.

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The role of clay minerals in formation of sliding surface – a case study of Črešnjevec landslide (Zagreb, Croatia)

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Črešnjevec is one of the largest and long-active landslides in southern hilly zone of Medvednica Mt. that belongs to residential area of the City of Zagreb and where the problem with landslides occurs for decades. The first activity of Črešnjevec was recorded in 1960s and it continues until today. According to MIHALINEC et al. (2002) the landslide body consists of Pliocene – Pleistocene and Upper Miocene sediments with sliding surface at approximately 12 m of depth in zone of contact between two mentioned types of sediments. The aim of this paper is to represent a mineralogical composition of sediments from Črešnjevec landslide to see whether or not a mineralogical composition, especially clay minerals, has an influence on physical and mechanical properties of landslide sediments making them sensitive to sliding. Because of different environmental conditions during the Pleistocene and Upper Miocene periods (KOVAČIĆ & GRIZELJ, 2007; GRIZELJ et al., 2017), it was expected that the mineral composition would be also different. Furthermore, it was assumed that samples from shear zone would contain expandable clay minerals and high values of Atterberg limits and external specific surface area. Mineralogical and geotechnical analysis were conducted on 15 samples collected from Črešnjevec 35 m deep borehole drilled in 2016. during the project of Detail Engineering Geological Map of Podsljeme urbanized area M 1:5000 – Phase II (MIKLIN et al., 2016), in which three types of sediments were recognized: (a) heterogeneous Pleistocene sediments, (b) red sandy clays of presumed Upper Miocene-Pliocene age and (c) silts and sandy silts of Upper Miocene age.

Atterberg limits were determined according to ASTM D 4318 – 10 (2010) standard proceeding. Residual shear strength parameters were obtained with standard direct shear test procedure. Specific surface area (SSA) was calculated from the Kozeny – Carman equation for hydraulic conductivity (URUMOVIĆ & URUMOVIĆ, 2016). Qualitative mineralogical analyses were performed by X-ray powder diffraction on random mounts of bulk samples and oriented mounts of <2 μm fraction. Oriented mounts of the <2 μm fraction were record after the following treatments: a) air drying, b) saturation with K^+, c) solvation of K^+ saturated mounts with ethylene-glycol, d) saturation with Mg^{2+}, e) solvation of Mg^{2+} mounts with glycerol, f) heating to 400°C and g) heating to 550°C. Semiquantitative mineral composition of samples was obtained based on interpretation of bulk diffraction patterns and data processing in “RockJock” quantification program (EBERL, 2003).

The main differences among all three sediment units are in carbonate and clay minerals content. Namely, heterogeneous Pleistocene sediments consist mostly of vermiculite, feldspars and quartz which are the main minerals in samples. Other mineral components in this unit are kaolinite, micas (illite and muscovite), goethite and amphiboles. Silts and sandy silts of Upper Miocene age consist mainly of quartz and micas in various quantitative ratios. They are in association with feldspars, carbonate minerals (dolomite, calcite), chlorite, smectite, kaolinite and goethite. Red sandy clays consist predominantly of quartz and micas in association with kaolinite, feldspar, goethite and small amount of vermiculite. Three of all samples match a shear zone with sliding surface. One of them is from units of heterogeneous Pleistocene sediments and other two from unit of red clays. They all have high clay content (38-76 %). The following mineral phases were detected in fraction <2 μm: kaolinite, mica and two types of vermiculite (one with diffraction maximum on 18 Å and other with diffraction maximum on 14.5 Å, after solvation of Mg^{2+} mounts with glycerol). Furthermore, these samples have the highest values of liquid limits (41-86 %) and plasticity index (22-49 %) as well as SSA (60-126 m^2/g) and very low residual shear strength parameters (c_{r1}=7 kNm^{-2}, c_{r2}= 6 kNm^{-2}, φ_{r1}=13.5°, φ_{r2}=11.2°). According to obtained results it can be concluded that clay mineralogy, as a result of different sedimentation conditions, obviously had great influence on formation of sliding surface.

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Removal of chromates and arsenates by halloysite-LDH composites

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Halloysite is a natural 1:1 layered aluminosilicate clay mineral belonging to the kaolin group which exhibits a unique tubular morphology. It has active surface hydroxyl sites which allow to attract ions from aqueous solutions due to protonation/deprotonation phenomena. Industrial activity often produces wastewaters containing anionic pollutants. These are hard to remove or neutralize by most of the mineral sorbents which usually have cation exchange properties. Previous studies indicated that halloysite could be used as a very promising material especially for removing As(V) from aqueous solutions (MATUSIK, 2014; MAZIARZ & MATUSIK, 2016). Typical sorbents capable of immobilizing anionic pollutants are rare and usually based on layered double hydroxides (LDH). The composition of these anionic clays is expressed by a general formula $[(M)^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}[A^{n-}{}_{x/n}\cdot yH_2O]$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively. The isomorphous substitution in octahedral sites of the brucite-like layers results in a net positive charge, which is neutralized by the hydrated anions occupying the interlayer space. A disadvantage of using LDH as a sorbent is their limited structural stability at low pH. Therefore, the aim of this work was to synthesize halloysite-LDH composites and to examine their sorption capacity towards As(V) and Cr(VI).

For this study halloysite sample was obtained from Dunino deposit located near Legnica in Lower Silesia (Poland). In turn, LDH of Mg-Al type was synthesized in laboratory by co-precipitation method. Raw halloysite and pure LDH were used for preparation of halloysite-LDH composites containing 5, 15 and 25 wt%. of LDH. The composites were prepared by two different approaches: direct precipitation of LDH in halloysite suspension and physical mixing of the two minerals. The sorption of As(V) and Cr(VI) was conducted for initial concentration of 1 and 5 mmol/L and initial pH 5. The suspensions (solid/solution ratio: 20 g/L) were shaken for 24 h at room temperature. Afterwards the anions concentration in the supernatant solutions was measured using colorimetric methods: molybdenum blue method for As(V) and diphenylcarbazide method for Cr(VI).

The XRD pattern of the halloysite sample showed a basal peak at 7.2 Å, which confirmed the presence of dehydrated halloysite-(7 Å). The basal spacing for pure Mg-Al LDH was equal to 7.7 Å which is in agreement with other studies indicating the presence of carbonates in the interlayer space. The IR spectra of the halloysite showed bands characteristic for kaolin group minerals related to the OH-stretching (3694 cm^{-1} and 3622 cm^{-1}). Additionally, the bands associated with stretching and bending vibrations of aluminosilicate framework (1200–400 cm^{-1}) were noticed. The IR spectra of LDH showed characteristic O-H and H_2O vibrations in the range of 3600–3300 cm^{-1}. The presence of carbonates balancing the structural charge was reflected by a band in the range of 1430–1350 cm^{-1}. The absorption bands at ~670 and ~550 cm^{-1} were attributed to Al–O bond and Mg-O vibrations. The XRD patterns of halloysite composites with LDH showed peaks which could be attributed to both phases. The LDH peaks intensity increased along with its content in the composite. The same observations were made for the absorption bands in the FTIR spectra.

The sorption capacity of all samples was very high regardless of the synthesis approach and the tested concentrations were much higher than those found in industrial wastewaters. The highest uptake of As(V) and Cr(VI) was measured for the pure Mg-Al LDH in the 5 mmol/L initial solution where it reached 255 mmol As(V)/kg and 250 mmol Cr(VI)/kg. An increasing content of LDH in composites caused an increase of sorption as compared to the raw halloysite, which adsorbed only 22.7 mmol As(V)/kg and 26.6 mmol Cr(VI)/kg from 5 mmol/L solution. This proves that sorption is mainly connected with anion-exchange of As(V) and Cr(VI) for CO_3. The sorption capacity of halloysite and halloysite-based composites was lower than that calculated for the LDH. However, the use of halloysite as a support for LDH aimed at increasing pH stability of the new hybrid sorbent.

Acknowledgments
This research was supported by the National Science Centre, Poland under the project no. 2017/27/B/ST10/00898.

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9th Mid-European Clay Conference – MECC 2018

Application of halloysite impregnated with Fe^0 particles for acid mine drainage water treatment

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In recent years, scientific interest in synthesis of pure metal particles has increased. This is mostly due to their possible application in catalysis and adsorption processes. However, it was found that the sole use of iron particles can be ineffective, as they tend to agglomerate, which results in loss of their reactivity (CHEN et al., 2011, XU & ZHAO 2007). Consequently, in recent years research involved the synthesis of Fe^0 composites, formed by coating various host minerals with iron particles. Since the coating with particles requires a large surface area of host to prevent aggregation, layered minerals can be successfully used for this purpose. This modification allows obtaining composites that exhibit outstanding adsorption properties, what facilitates their application in wastewater treatment. The problems of acid mine drainage water (AMD) affects many countries with developed metals and coal mining industry. Due to wastewater properties, in particular presence of many chemically different substances, the AMD treatment poses challenge for searching and elaboration of new, simple methods for wastewater treatment. In present study, the Fe^0 particles were synthesized and simultaneously deposited on halloysite (H) surface. The research objective was to evaluate the adsorbents efficiency in the removal of inorganic ions from AMD, collected from quartzite quarry, located in the western part of the Świętokrzyskie Mountains, near Kielce city in Poland. In particular, the efficiency of As(V), V(V) and S(VI) removal by the Fe^0 composites was studied, due to its increased concentration in the studied AMD.

For a study, naturally occurring halloysite from Polish deposit Dunino (south-west Poland) was used as support for Fe^0 particles. The mineral samples loaded with Fe^0 particles (HFe^0) were synthesized by reducing Fe-precursor in ethanol solution. As the Fe-precursor and reducing agent $FeCl_3 \times 6H_2O$ and $NaBH_4$ were used, respectively. The resulting black solid was washed with ethanol and dried at 60°C. The above synthesis procedure involved different loadings of Fe^0 particles on layered minerals surface. These were adjusted to 10 wt% ($HFe^0 10$) and 25 wt% ($HFe^0 25$). The adsorption properties were studied in the function of composites dosage (0.5–20.0 g/L), using batch-adsorption techniques in static conditions at room temperature (22°C). The concentration of the ions before and after adsorption experiments was analyzed using ICP method.

The XRD patterns of studied composites revealed major basal spacing at approximately 7.18 Å, which is attributed to halloysite mineral phase. After loading with zero-valent iron particles, the position of halloysite basal reflection did not change, confirming that the interlayer space was not altered. In turn, reflection at 2.03 Å was observed, attesting successful formation of Fe^0 particles exclusively on the halloysite surface. It was noticed that the intensity of the reflections attributed to the Fe^0 formation increased with the increase of Fe^0 particles' loading. The FTIR spectrum showed lack of structural perturbations within the 1:1 layer which was in agreement with XRD results. Apart from the particles, recognized as zerovalent iron, the SEM images showed fibrous phase covering the halloysite particles, which was recognized as iron oxyhydroxide (Fe(O)OH). This confirmed that Fe^0 underwent partial oxidation in the applied experimental conditions. The AMD analysis revealed, that initial As(V), V(V) and S(VI) concentration was equal to 24.2 mg/L, 0.39 mg/L and 1810 mg/L, respectively. The adsorption results showed, that the highest efficiency in As(V) and V(V) removal was determined for the $HFe^0 25$ sample. The adsorbent dosage experiments revealed that its dose of 10 mg/L is sufficient to decreased As and V concentration below detection limit (<0.15 mg/L and 0.05 mg/L, respectively). In this case the initial pH of 2.15, increased to 4.24 after treatment. However, the S concentration remained high, through the studied dosage range. The lowest concentration was determined at dosage of 20 mg/L and was equal to 1390 mg/L.

The results allowed to conclude that, $HFe^0 25$ composite can be used as effective adsorbent in As(V) and V(V) removal from AMD. However, the low efficiency in S removal indicated that treatment conditions need to be optimized. Since, the presence of organic matter in water solutions can significantly influence the adsorption processes, it has to be thoroughly investigated. These may be connected to binding of metal ions to humic substances. Therefore, in the next step of research, experiments involving supporting treatment process as coagulation-flocculation of humic substances present in AMD will be studied. As well as, in particular, the adsorption mechanisms involved in inorganic pollutants removal by the Fe^0 composites will be examine.

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Mathematical model of methylene blue dimerization on clay surfaces

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Methylene blue (MB) is a cationic dye which diluted into a solution forms aggregates. Increasing of the concentration can form different molecular structures especially when they are interacting with charged clay surface (BERGMAN & O`KONSKI, 1963; BUJDAK et al., 2003; MILOŠEVIĆ et al., 2013). Diffuse reflectance (DR) spectroscopy represents an important method in mineral diagnostics (CLARK, 1995) and it can be used as a method to gain information about aggregation of MB molecules on the surface of clay minerals (MILOŠEVIĆ et al., 2016). The main goal of this study is to present a mathematical model to determine the point of dimer formation based on the data obtained from DR in the near-infrared (NIR) region.

Investigation was carried out on different types of clays from Serbia: montmorillonite, mixed-layer smectite-illite and kaolinite-illite. Kaolinite from Sedlec (Czech Republic), was used as a reference for kaolinite. Samples were prepared with MB solutions and transferred on the microscopical glass slide as described in MILOŠEVIĆ et al. (2016). DR data were measured in the NIR region (1300–1500 nm) with two different angles of the polarised light, parallel and at 45°, in regard to the surface of the samples. ExpAssoc function of the OriginPro8.5 was used for the modelling of the obtained data. Saturation of cationic exchange capacity (CEC) of the samples by addition of different concentrations of MB solution leads to decrease of the intensity of the main OH vibration band (around 1410 nm) in regard to the raw samples. Kaolinite clays show less pronounced dependence on the angle of the polarized light in regard to smectite clays. Aggregation of MB molecules can be described by a mathematical model. ExpAssoc function ($Y=Y_0+A_1*(1-e^{-x/t1})+A_2*(1-e^{-x/t2})$) gives results that are in a good agreement with measured data ($R^2>0.9$). When the value of the first derivate of this function reaches zero process of dimerization is finished. After this point formation of higher molecule aggregates is possible. In case of higher charged clays derivative function reaches zero at low concentrations of the MB solution and the dimerization is finished quickly which is in correlation with the literature data (KLIKA et al., 2007). Process of dimerization for the low charged clays is not finished in the measured range of the concentrations but the model can be extrapolated to the higher concentrations so it gives a probable point where the higher aggregates are formed. Aggregation of monomers into dimmers occurs in a fast rate with adsorption on the surface and furthermore leads to cationic exchange and adsorption in the interlayer. It is a result of the surface adsorption and it depends on the charge density of the clay. In the kaolinite clay this aggregation is forming in a slow rate and reaches zero when the CEC is almost completely saturated so formation of higher aggregates is unlikely to happen in high amount. In case of higher charged clay (smectite) aggregation occurs faster and the formation of higher aggregates can start with the CEC saturation of 10 %. These data highly depend on the type of the clay but the model can provide information for a clear distinction between different types of surface charges of the clay.

For a better understanding of dimer formation and a more precise mathematical model including the changes it is necessary to perform additional studies with different types of clay minerals.

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The present study was supported by the Ministry of Education and Science, Republic of Serbia, Project no. 176010.

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Removal of iron during bleaching of Bulgarian kaolins

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Brightness improvement is important for increasing kaolin's value. In this study, the occurrence of iron in Bulgarian kaolins, the current technology in bleaching kaolin at KAOLIN EAD company and alternative processes for iron removal during bleaching have been briefly analyzed and compared.

Main colouring oxides in kaolin composition are Fe_2O_3 and TiO_2. The main phases which bind Fe_2O_3 in the Bulgarian kaolins are micas, iron oxides and iron oxyhydroxides. Bulgarian kaolins are characterized by relatively low content of TiO_2 (< ~ 0.5 %) and are free of organic matter. The most common methods for chemical reduction of iron are acid bleaching, hydrosulphite reduction, reduction by sodium borohydride, thiourea dioxide etc. Nevertheless, these methods do not substantially increase the brightness of the bleached kaolin relative to kaolin's brightness obtained with hydrosulphite reduction, which is the basic technology of the KAOLIN EAD company. In addition, the prices of the applied reagents are comparable or exceed that of the sodium dithionite, and magnetic separation of our kaolin grade has a relatively slight effect on the brightness of the kaolins, because of the mineral form of the iron-containing compounds in these kaolins. Optical bleaching is a comparatively less studied method for improving brightness of kaolin grades. On processing the Bulgarian kaolins with cationic dyes, materials of similar brightness, and lower yellowness (by around 1–2 %), at a relatively low cost, are produced.

DFT study of atrazine-beidellite intercalate

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One of the most employed pesticides is the atrazine, belonging to the s-triazine family. It has a negative impact on the environment and health (BELZUNCES, et al., 2017). Clay minerals, e.g. montmorillonite or beidellite are suitable candidates to immobilize organic contaminant, like atrazine, e.g. from waste water.

These clays are highly hydrophilic and consequently show very limited adsorption capacities for hydrophobic organic contaminants. However, a higher adsorption of organic molecules/cations can be obtained by modifying of the clay surface by organic surfactants (GRUNDGEIGER, et al., 2015).

The Density Functional Theory (DFT) D3 method with employed dispersion corrections (GRIMME et al., 2010) was used for study of interactions in the atrazine-beidellite (A-Bd) structure. Two models were proposed: 1. Atrazine intercalated in the Bd interlayer space (A-Bd), and 2. A-Bd together with the tetramethylphosphonium (TMP) cation as an organic surfactant in the interlayer space of Bd (ATMP-Bd).
Beidellite is aluminosilicate with predominant substitutions in tetrahedral sheets versus in octahedral ones in montmorillonite. This different charge distribution in beidellite improves a stability of prepared organoclays (SCHOLTZOVÁ & TUNEGA, 2017).

The vibrational spectra obtained from *ab initio* molecular dynamics calculations were analyzed in detail and compared with measured FTIR spectrum of the synthetized A-Bd organoclay.

Acknowledgements
Authors are grateful for the financial support by the Slovak Research and Development Agency (APVV-15-0741 and APVV-15-0479).

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The influence of zeolites from Donje Jesenje area on the removal of lead and cobalt from water

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Zeolites are minerals from the aluminosilicate group. They have an important role in water purification processes because of their latticed structure which enables cation exchange and adsorption of heavy metal cations (WANG & PENG, 2010). The basic units in the three-dimensional structure are SiO_4 and AlO_4 tetrahedrons with cavities and channels inside. The cation exchange capacity primarily depends on the degree of isomorphic substitution of Si^{4+} cations with Al^{3+} cations in the tetrahedron, which creates the negative surface charge. In order to neutralize the negative charge the alkali and alkaline earth cations such as Na^+, K^+, Ca^{2+} and Mg^{2+}, are incorporated into the structural grid. Cavities also contain zeolite water which is easily removed by heating to several hundred degrees Celsius; the dehydration temperature depends on the type of zeolite.

The zeolite tuff which belongs to volcanoclastic deposits of the Lower Miocene from an abandoned quarry from Donje Jesenje area was used in the research. The X-ray diffraction analysis (XRD) indicates that the main component is one mineral from zeolite group – clinoptilolite (>50 %). The secondary components are other minerals from zeolite group such as mordenite and stilbite, and feldspars from plagioclase group, quartz and illite. The clinoptilolite is a product of alteration of volcanic glass at elevated temperature caused by burial diagenesis (TIBLJAŠ & ŠĆAVNIČAR, 2007).

The distilled water with dissolved salts of lead and cobalt of known concentration was used in the experimental part. The tuff was crumbled and sieved before the heating in the oven on the temperature of 110-120ºC to remove the zeolite water. The natural zeolite and the one previously treated with HCl acid, for elevating the efficiency of adsorption processes, were used for water purification (OLA et al, 2013). The zeolite was added to the aqueous solution to react for 30 minutes and then the filtration was carried out. After the separation of solid phase, water analysis was carried out to determine the concentration of lead and cobalt.

The aim of this research is to determine the degree of lead and cobalt removal from water with the use of natural zeolites from Donje Jesenje area. The comparison of the adsorption capacity of natural zeolite and the one previously treated with acid is also important.

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Detailed study on origin, geology and mineralogy of Ahırözü Kaolin Deposits, Mihalıççık, Eskişehir-Turkey

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There has been no detailed known research related to the occurrence and origin of the Ahırözü kaolin deposits located in Mihalıççık, Eskişehir. Turkey is composed of several continental sectors combined together into a single landmass in the Late Tertiary (OKAY, 2008). The Sakarya terrane, in which the study area is situated, extends from the Aegean region of Turkey from the west to the Eastern Pontides (OKAY, 2008). The Sakarya terrane includes Variscan metamorphic sequence composed of gneiss, amphibolites, marble and metaperidodite (OKAY, 2008). The basement rocks in the study area consist of Early to Middle Triassic blue-green schists, gneiss and marbles, and Late Triassic serpentinite rocks, while Late Triassic granitic units are exposed to the south of Hamidiye village and Early-Mid Triassic blue-green schists and marble as metamorphic units are observed to the north of Hamidiye village (GÖZLER, 1987; KARAKAŞ, 2006).

Based on the field observations, mineral associations and textures, the original rocks exposed in the study area have been identified as basic and felsic igneous varieties and metamorphic rocks. Dominantly, five different secondary mineralization products have been detected as clay, chlorite, listwanite, carbonate (i.e. dolomite) and amorphous silica. Secondary quartz crystals fill the stockwork type microfractures of the host rocks as a result of the precipitation of excess silica in the system. Therefore, two types of alterations related with these mineralization processes have been determined in the study area, namely; argillic and propylitic. The mineral paragenesis of argillic alteration is composed of kaolinite, smectite, illite, natroalunite in addition to the accessory minerals which are identified as dickite and pyrite. This mineral paragenesis correspond low-intermediate argillic alteration caused by chemical fluids having neutral to acidic pH with low temperature values less than 200ºC.

In order to verify alteration zones exposed in the study area regarding to the chemical analyses, two types of alteration index equations which were Ishikawa Index (AI) and chlorite-carbonate-pyrite index (CCPI) were used. The main purpose to use these equations was to detect the alteration types occurring in the study area. Serpentinized rocks were mainly dolomitized whereas metamorphic originated wall-rocks were dominantly altered into chlorite according to the calculations indicating the entity of propylitic alteration. However, the rock-samples acquired within the deposit itself were identified as hydrothermally altered kaolinized rocks. Stable isotope analyses (oxygen/hydrogen) stated that the rocks were mainly interacted with surface waters in which 8 kaolinized rock-specimens fell into the area comprising the clay and aluminium-iron hydroxide sector between kaolinite and montmorillonite lines. Conversely, only one sample indicated a magmatic water source interaction into the system.

The mineralogical and geochemical investigations of the Ahırözü kaolin deposits in the Mihalıççık-Eskişehir area demonstrate that they are the products of hydrothermal alteration of granitic intrusives emplaced in a volcanic arc related tectonic setting. The kaolin samples are characterized by depleted Rb, Pb and Y in contrast to the enriched Cs, U and Sr elements. These variations may either be inherited from the parent rock, or probably the abundances of the trace elements, especially large ion lithophile (LILE) elements in major silicate minerals such as feldspar and mica, are mobile during hydrothermal alteration. Based on the fluid inclusion data and stable isotope analyses, intense silicification and sinter formation related to mineralogical zoning and lack of pyrophyllite mineral (HEDENQUIST et al., 2000), it can be suggested that low sulfidation supergene alteration in an epithermal system was active in the study area.

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This study was financed by METU- BAP-07.02.2012.101 and METU-BAP-03-09-2013-001.

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Removal of heavy metals from polluted soil using zeolites synthesized from perlite by-product material

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The fine powdered perlite, a by-product of processing of raw perlite from the Lehôtka pod Brehmi deposit (Slovakia), was used in the present study as a starting material for zeolite synthesis. Currently, this material has very limited application (only as a partial replacement for cement in concrete). The conversion of fine perlite by-product material (PBM) into zeolites is proposed to recover this material and to obtain value-added material with attractive sorptive properties. Zeolite synthesis was performed in batch experiments in a wide range of experimental conditions (temperature, time, NaOH concentration) and the reaction products were characterized for their mineralogy, chemistry and surface properties. The pollutant removal efficiency of the synthesized zeolitic materials was assessed by sorption experiments using pore water obtained from a soil contaminated with heavy metals (mainly Zn and Pb). The main goal was to find a relationship among the synthesis conditions, properties of synthesized zeolitic materials and pollutant removal efficiency in order to minimize the accumulation of perlite by-product by its transformation to added-value material and propose possible application for the synthesized zeolitic materials.

For the batch experiments, 11 g of PBM (<63 μm) was placed in polypropylene bottles and 80 mL of 1–5 M solution of NaOH was added. The bottles were closed and kept at 50–80°C for 24–144 h, and then the solid products were separated by centrifugation. The chemical composition of the reaction solution was determined by ICP. The solids were washed by distilled water until the pH was below 10. Then the solids were treated with 1 M NaCl and the excess soluble salts were removed by centrifugation followed by dialysis. The Na-saturated solids were dried and analyzed by quantitative XRD, FTIR, SEM-EDX, specific surface area, CEC and zeta potential. For the sorption experiments, soil pore water (SPW) obtained from highly metal-contaminated alluvial soil from Příbram District (Czech Republic) was used. A mass of 0.02 g of Na-saturated zeolitic material was placed into a 15 mL polypropylene tube and 10 mL of SPW was added to maintain the L/S ratio of 500 L/kg. Six time steps (10 min, 30 min, 1 h, 2 h, 6 h and 24 h) were run in duplicates under continuous shaking at 24°C, followed by centrifugation and filtration. The leachates were analysed for major and trace elements using ICP-OES.

The preliminary results showed that the PBM consisted of 96 wt% of volcanic glass and minor amounts (4 wt%) of mica, feldspars, quartz, and sometimes opal-CT. The accessory minerals (mica, feldspars, quartz and opal-CT) were not affected by synthesis. They were identified in all reacted samples along with variable amounts of unaltered volcanic glass and reaction products i.e. zeolites. With increasing NaOH concentration, temperature and time the dissolution of volcanic glass increased and, larger amounts of zeolites were formed. The PWBM reacted with 5 M NaOH solution for 144 h at 80°C contained only 16 wt% of unaltered volcanic glass and 77 wt% of synthesized zeolites. The main zeolite reaction products identified by XRD were zeolites X, P and phillipsite while sodalite was present in traces. The experimental conditions had a significant impact on the type and quantity of synthesized zeolites. Phillipsite, zeolite P and zeolite X were preferentially formed after reaction of PBM with 1 M, 3 M and 5 M solution of NaOH, respectively. The synthesized zeolitic materials showed contrasting physico-chemical properties (e.g. specific surface area and CEC) mainly due to the variable zeolite content and distinct structural features between zeolite species. Similarly, the synthesized zeolitic materials showed different efficiencies in removal of heavy metals from SPW. Zeolite X-rich material removed >94 % of Zn from the SPW whereas zeolite P-rich and phillipsite-rich materials removed 87 % and 35 % of Zn, respectively. The higher Zn removal efficiency for zeolite X might be related to the larger dimensions of structural channels within zeolite X framework compared to those of phillipsite and zeolite P.

Acknowledgments

The authors are grateful to the Slovak Research and Development Agency (project APVV-0339-12) for financial support and LBK PERLIT, s.r.o for providing samples.

Geochemical and mineralogical signatures of Istrian Lower Palaeogene bauxites – a geodynamical thread

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Bauxites are recognized as regional markers of global events that occurred in specific intervals in the stratigraphic record when warm and humid climate was combined with tectonically controlled subaerial exposure of the carbonate platform (D'ARGENIO & MINDSZENTY, 1995). A general consensus has been reached in the geological community in favour of their polygenetic nature (MINDSZENTY et al., 1995), implying karstification prior to deposition and transformation of the soil-derived proto-bauxite material (terra rossa) (DURN et al., 1999). However, the issues concerning the eventual source of the parent material (residual vs. detrital origin) is still much debated and recently deepened with another theory of terra rossa formation, namely the concept of isovolumetric reaction between the carbonate bedrock and airborne material at a narrow reaction front, proposed by MERINO & BANERJEE (2008) and developed by BANERJEE & MERINO (2011). In this light the replacement of calcite by clay results with the formation of authigenic red claystone subsequently pedologically altered into a soil (terra rossa). This paradigm shift sees the terra rossa as the proto-bauxitic material coupled and mutually reinforced with karst weathering that occurs at its base, an issue not considered previously by proponents of detrital theory, let alone the residual one.

In Istria, the bauxites occurring at the regional K–Pg unconformity were studied at large by ŠINKOVEC (1973). The bauxitiferous area extends from Umag to Labin in approximately 60 km long and 4 to 6 km wide belt, including the western parts of the Učka Mt. The single ore bodies are rather small, conical in shape, with surface outcrops mostly 100 to 300 m^2 and depths 8 to 30 m. In the great majority of cases the bauxite deposits are preserved on the exhumed Cretaceous stratigraphy as the Lower Palaeogene (Eocene) hanging-wall sediments are completely eroded, leaving the outcrops covered by terra rossa. Their concentration may be high, often containing 10 to 90 deposits at one 1 km^2 of the land surface. Earlier investigations (ŠINKOVEC, 1973; KOVAČEVIĆ GALOVIĆ et al., 2012) showed that the chief mineral is boehmite, followed by hematite, while the content of kaolinite is rather irregular. The investigation of the vertical cross sections (ŠINKOVEC, 1973) indicated that, in general, the distribution of trace elements in the deposits was uniform. More recent investigations (PEH & KOVAČEVIĆ GALOVIĆ, 2014, 2016) demonstrated that discontinuity surface underlying Istrian Lower Palaeogene bauxites was characterized by diachronism caused by development of the flexural forebulge on the Istrian Karst unit (sensu KORBAR, 2009) facing the approaching orogen (High Karst unit). Forebulge evolution is recorded in geochemical signature of bauxite deposits overlying one of four Lower–Upper Cretaceous formations (Pula–Rušnjak–Sveti Duh–Gornji Humac). It gives the Sveti Duh bauxite group a pivotal position in the significant geochemical (Cr/Ni) partitioning after the initial input of source material (Gornji Humac). Bauxite-hosting Sveti Duh and Rušnjak formations mark the stage of maximum possible uplift and erosion, facilitating maturation of the proto-bauxitic material under oxidizing, vadose conditions. On the contrary, the Pula group is formed on the distal flank of the forebulge (away from the orogenic wedge), and provides the evidence of geochemical signal characteristic of reducing environmental conditions.

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Detection and quantification of TiO_2 polymorphs in kaolins by X-ray diffraction

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The minerals anatase, rutile and brookite (the common polymorphs of titanium dioxide (TiO_2)) are not uncommon minor/trace components of many clay materials such as kaolins. Following the proposal by the French Agency for Food, Environmental and Occupational Health & Safety (ANSES), on behalf of the French Member State Competent Authority (MSCA), to the European Chemicals Agency (ECHA) for TiO_2 to be classified as a Category 1B carcinogen by inhalation (ANSES, 2016) and subsequent proposal to classify TiO_2 as a Class 2 carcinogen (EUROPEAN CHEMICALS AGENCY, 2018), there has been increased interest in accurate quantification of anatase, rutile and brookite in industrial clay materials.

Anatase and rutile are very good diffractors with nominal, peak area based, reference intensity ratios (I/Icor) of 4.3 and 3.4, whilst for brookite the value is around 1.6. Hence with appropriate sample preparation and good counting statistics, analysis by X-ray diffraction (XRD) can obtain lower limits of detection for anatase and rutile that are routinely in the sub-percent range, with anatase being the most readily detectable of the three polymorphs. In a practical sense, however, detection and quantification of the TiO_2 polymorphs in kaolins is often affected by line overlap with other minerals present, not least for example the 002 peak of kaolinite itself which may effectively mask the main anatase peak at 3.52 Å. Quantification after dehydroxylation of the kaolinite to metakaolin is an effective strategy in many instances to deal with this overlap but other peak overlap issues may remain that must be considered when choosing which XRD based quantification approach to adopt.

A survey of a range of common kaolins indicates that either anatase or rutile may be the most abundant polymorph, whilst brookite is less commonly encountered, perhaps not simply just because it is less readily detected by XRD. Ball clays in particular seem to most commonly have more rutile than anatase, whereas in other kaolins it is typically anatase that is most abundant. However, it is not known if this observation is related to the limits of the survey or is a more general feature of this type of clay.

Comparison of polymorph quantification by XRD to total TiO_2 determined by chemical means is in reasonably good agreement across all kaolin types, but typically there is a small shortfall which may suggest minor TiO_2 is also commonly present in other forms.

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Influence of organic matter on soil mechanical properties

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Soils are the largest terrestrial reservoir of organic carbon. Many investigations are carried out from the point of view of the CO_2 cycle and touches topics like the special association and interaction behaviour of (clay) minerals with organic matter (OM) and the stabilizing mechanisms of OM in soils. Mineral surfaces in soils, sediments, and aquatic systems are often coated to a large extent with natural OM, such as humic substances. In particular, clay minerals provide effective surfaces for stabilizing OM (CHEN et al., 2017; CHOTZEN et al. 2016). It is obvious that such coatings/associations will affect the soil mechanical behaviour of clayey soils, e.g. by decreasing shear strength and plasticity. This fact has also been included in the geotechnical classification of cohesive soils based on the decrease of the plastic limit after drying (SN 670 004-2b) or on the loss on ignition (EN ISO 14688-2). Furthermore, the influence of organics on the soil mechanical properties is widely applied in construction engineering. The supporting function, viscosity and thixotropy of slurries in diaphragm walls or slurry shield tunnelling are improved by admixing of polymers and fillers (HEINZ et al., 2004). For tunnelling using earth pressure balance machines in clayey soils the addition of conditioning chemicals (e.g. foams, polymers, and polyamines) transforms the excavated material into a deformable soil paste with preferably low strength, adhesion and clogging potential. The mechanism is based on sealing the clay aggregates against the penetration of water (ZUMSTEG et al. 2012, 2013).

Nevertheless, for natural soils, systematic studies on the influence of OM on soil mechanical properties such as compressibility and shear strength are poorly studied. An increasing compressibility of different with humic acid reconstituted clays based on consolidation tests was found (ZENG et al., 2017).

The paper presents results of studies on the influence of various organic substances (humic acid and cellulose mimicking natural OM) on the mechanical properties (plasticity and shear strength) of various clays (kaolin, illite, and bentonite) and natural soils.

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pH-dependent silica dissolution and rheology of Na^+-montmorillonite water dispersions

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One of the most important field of application of clay minerals is their use as rheology control agents. In the water media smectite particles such as montmorillonites (MMT) could swell significantly to form the few types of colloid structures (LAGALY, 2013; VAN OLPHEN, 1991) performing different physico mechanical properties. Special ability of bentonite clays from different deposits to form water-based drilling muds depends dramatically on the outer conditions, e.g. salinity and ions nature, clay particle concentration et cetera. pH level also imparts grand diversity for the clay dispersion structures and properties. Usually this factor is considered in the context of negative edge charging, ion exchange, ionic strength increasing. But the role of labile colloid silica dissolution/adsorption under different pH conditions has not sufficiently been taken in consideration.

As it is known Na^+-MMT`s dispersions keep some buffering properties at near neutral pH and its dispersions rheology is controlled mainly by the water salinity. The structure of dispersions is represented by the number of face-to-face, edge-to-face and edge-to-edge contacts between the particles. In the case of alkali electrolytes like NaOH and Na_2CO_3 additional interactions take place in systems - anions adsorption, hydrolysis, ionic exchange with H^+-cations and silica dissolution. The rheology of dispersions after sodium activation changes and become time dependent.

Two perspective bentonite deposits with high-smectite content were taken as the source of MMT particles–Tagansky (Ca^{2+}, Mg^{2+}-bentonite, Republic Kazakhstan) and Dash-Salakhly (Na^+, Ca^{2+}-bentonite, Republic of Azerbaijan) supported by Russian “BENTONITE Company” LLC. Activation was performed by NaCl treatment and subsequent washing from electrolyte excess by centrifugation. Stock dispersions obtained contain about 2.5–4.0 wt% of MMT and 7–10 mM of NaCl. ZetaSizer (Malvern) was used to get particle size distribution (PSD) and ξ-potential of MMT particles in diluted dispersions. Brookfield R/S plus rheometer with cylindrical geometry was used to provide rheological measurements of concentrated dispersions. Photometric molybdate method was used to check amount of soluble silica and molecular mass distribution (MMD) of silicic acid polyanions (PSA) after addition and during the aging of MMT dispertions under pH control.

When pH level increased some structure plastification occurred in NaOH containing systems and different level of structure reinforcements was founded in the NaCl and Na_2CO_3 containing dispersions (Fig. 1).

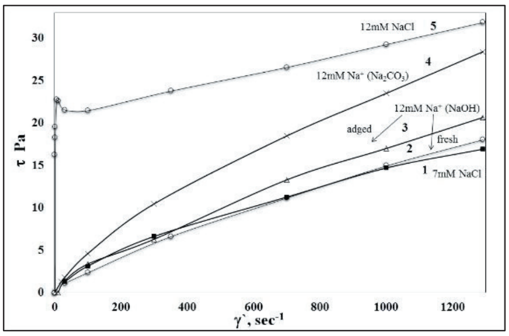

Figure 1. Flow curves of 2.5 % water MMT dispersions:1 - initial system (7 mM NaCl), 2–1 day after addition of NaOH (12 mM Na^+), 3–7 days after addition of NaOH (12 mM Na^+), 4–1 day after addition of Na_2CO_3 (12 mM Na^+), 5–1 day after addition of NaCl (12 mM Na^+).

At the first time after NaOH addition pH value increase and then falls to the initial level. In the case of Na_2CO_3 pH value remain in the alkali zone. Simultaneously silica dissolution takes place. Silica concentration in water changes non- monotonically with time, and its maximal amount is proportional to the pH level. MMD of PSA is changed with time from small to high polymerization degrees and then it returns to the initial level. At the same time no major changes in PSD and electrokinetic potential values in diluted dispersions were found at high pH despite the strong changes in rheology. In this report the role of water soluble silica in MMT dispersions structuring processes is discussed.

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Structural description and properties of Mg_2Al-layered double hydroxides intercalated with the fluvastatin anions solved by molecular simulation methods

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We present the structure analysis of Mg_2Al layered double hydroxides intercalated by fluvastatin anions based on published experimental data and show the advantages of molecular simulation methods for description of complex organo-clay hybrid materials. Models with different arrangements of intercalated fluvastatin anions, which fully compensate the positive charge of the LDH layers, were calculated. All presented models were analysed by calculated XRD patterns, basal spacing, and free volumes calculations to describe different behaviour and properties between individual models with different arrangement of the fluvastatin anions. Based on total energy values bilayer and pseudobilayer models are preferred with respect to monolayer models. Calculated results were thoroughly compared to published experimental data and a detail comparison between experimental and calculation X-ray data is presented. It was shown that calculated patterns for monolayer and bilayer arrangement do not reach a good agreement with experimental diffraction data so as the basal spacings. In opposite of this calculated XRD patterns proved a pseudobilayer arrangement with mixture of flat and tilted positions of fluvastatin anions in the interlayer space as well as equal distribution of water molecules in the interlayer among fluvastatin anions.

Acknowledgments
This study was financed by the Charles University, project GA UK No. 294215.

LDH as a drug nanocarrier described by DFT and MD calculation methods

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We report results based on the classical molecular dynamic (MD) and density functional theory (DFT) study of Mg_2Al layered double hydroxides (LDH) intercalated with two drugs – mefenam acid and sulindac. These drugs have anti-inflammatory and anti-nociceptive effects (anti conduction of painful stimuli). The series of models with different amount and initial arrangement of intercalated drug were built and analysed in order to compare the calculation results with experimental data published in CUNHA et al. (2016) and ROCHA et al. (2016). DFT calculations were carried out in QuantumEspresso and MD calculations in Materials Studio software package.

Comparison of calculated XRD patterns, basal spacings, concentration profiles, free volumes and mean square displacements will be presented for LDH supercell with total surface area of 400 Å^2. DFT calculation were used for studying of interactions between LDH surface and drug. The whole complex structure was analysed by MD calculation on ns time scale. Results for modified forcefields in comparison with DFT substructure calculation and experimental results will be presented.

Acknowledgments

This study was supported by the Charles University project GA UK No. 194217.

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Benefits of 3D X-ray tomography (XCT) analysis on textural bentonite characterisation

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Detailed investigations regarding bentonite genesis and subsequent alteration are utilised in enhancing conceptual understanding of the behaviour of bentonite based engineered geomaterials in the long-term. This is of special interest in the field geological disposal of long-lived hazardous waste (e.g. spent nuclear fuel) where the behaviour of the used materials needs to be understood over geological timescales (up to ~1 Ma; e.g. POSIVA, 2017).

The fast/extensive applications of conventional methods of describing composition and textures of bentonite (or any other clay deposits) are often limited by the number and amount of samples. Information obtained is often from a small sample / processed material to represent bulk conditions (e.g. XRD analysis), or a 2D characterisation of a limited area and even more limited volume (thin section). Reasonable spatial coverage of analysis requires extensive sampling since clay materials often show no visible changes to the eye, even when their composition might change. To increase the ability to produce more continuous information requires quicker and simpler methods to allow more coverage and 3D information. In addition, quick scanning of e.g. drill core samples provides a better means of sample targeting for conventional analyses.

It is acknowledged here that, for quick scanning of chemical change, methods like portable XRF or hyperspectral (e.g. SUN et al., 2017) methods have the potential to be utilised more. However, here the main focus is set on textural characterisation. X-ray tomography (XCT) provides a non-destructive and relatively quick method that can be utilised to describe textural variation in bentonite (and other clay) materials. It works especially well for drill core samples. Here, benefits of utilising XCT are discussed through analysis of samples from the Kato Moni bentonite site in Cyprus, which has recently been thoroughly examined with more conventional methods (ALEXANDER et al., 2017).

This presentation focuses on the benefits of including XCT analysis in the investigations and describes best ways of utilising this method to support deposit scale characterisation, as well as other possible research applications related to radioactive waste disposal engineering. Sampling techniques and their significance for the results are also discussed. This is of increased importance when dealing with potentially swelling materials as conventional sampling methods inevitably lead to heave of the confined swelling clays. This needs to be accounted for when analysing *in situ* density, but also when interpreting textural information. In addition to expansion, sample drying creates fractures that have to be accounted for during textural interpretation. Both heave and drying can enhance some structural features and thus be beneficial for the interpretation. However, if *in situ* textures of bentonite deposits need to be examined, sampling needs to be carefully planned to preserve *in situ* pressure and water content. Sequential pressure release, or drying, of samples could also be used deliberately to observe certain features and planes of weaknesses in swelling clay materials.

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Ethnopharmacological use of geophagic clays

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Clays are the dust of the Earth. The ubiquitous presence of minerals in the environment exposes humans to its effects, both positive and negative. Concerning the positive aspects, it is already a common concept that the human body requires chemical elements such as Ca, Mg, K and Na, in levels which may be considered high, which can be obtained by clay minerals. However, they can also represent a risk of toxicity, depending on the dose and may even be lethal.

Clays have also been traditionally used as food supplements and dressings (primarily for gastrointestinal problems) and continue to be so in many contemporary societies. Aristotle made the first reference to the human deliberate eating of clay for therapeutic purposes. The famous "Armenian Bole" was a soft red clay prescribed against diarrhoea, dysentery and haemorrhage. Galeno described the "medicinal terras" used mainly for gastrointestinal affections, and Avicena mentioned the use of clays for anti-poison treatments. Paracelsus used minerals for drugs preparation and these played a relevant support for his creation of what he called Iatrochemistry, a proto-Pharmacology.

Geophagy is the practice of eating terrestrial substances (such as clay), often to improve a poor mineral nutrition. The intake of minerals and chemical elements through water, soil (through geophagy) or dust can be accomplished by ingestion, inhalation or dermal absorption. It is generally assumed that geophagia can help supplement mineral nutrients. Mud/clay can be prepared in the form of cookies, sometimes called "bonbon de terre", which are sun-dried and sold throughout the poor areas. Small quantities of other ingredients such as salt and vegetables, sometimes sugar, are added.

A recent trend in scientific research is to study geophagy not as pathology, but rather as an "adaptive behaviour", supplementing the diet with essential nutrients or treating a disorder (e.g. diarrhoea).

Special clays, such as bentonite, are available throughout the world as a digestive aid. Another special clay, kaolin, is also widely used as a digestive aid and as the basis for some medicines and feed. Attapulgite, another special clay, is used as an active ingredient in many anti-diarrhea treatments. The composition of these materials can be so variable that when consumed by humans, special attention should be paid to their chemical and mineral composition.

The future of geophagy depends on scientific support and the establishment of quality standards and protocols to reassure public opinion and regulate markets.

More recently, clays/clay minerals are used as active ingredient, namely as gastrointestinal protectors, laxatives and antidiarrheals; as excipients, supporting various substances with bioactivity, improving organoleptic characteristics, facilitating the preparation and/or promoting the disintegration of the active product. Clays are described as modulators of several systems of drugs release, e.g. ibuprofen. The inclusion of clays in (nano-)composites reveals improvements of mechanical properties and polymer materials, opening ways for development of new materials for biomedical applications.

Acknowledgments

Supported by GeoBioTec Research Centre (UID/GEO/04035/2013), funded by "Fundação para a Ciência e Tecnologia" (FCT, Portugal), FEDER funds through the Operational Program Competitiveness Factors COMPETE. FCT granted the third and fourth authors a PhD scholarship (SFRH/BDE/11062/2015 and SFRH/BD/102837/2014).

The influence of Fe-oxides and organic matter on surface properties of nanostructured microaggregates of the Terra rossa and Calcocambisol

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This study investigates the influence of Fe-oxides and organic matter on surface properties of nanostructured mineral microaggregates obtained from the Terra rossa and Calcocambisol developed on hard limestone and dolomite in Istria, Croatia.

The mineral composition and the morphology of samples (B horizon) were investigated using X-ray diffraction and field emission scanning electron microscope (FE-SEM), respectively. In order to determine the influence of Fe-oxides and organic matter coatings on surface properties of soils, samples were selectively dissolved. Particle size distribution, specific surface area (SSA), and electrophoretic mobility (EPM) were measured on the following soil subsamples: original samples, samples treated with H_2O_2, samples treated with H_2O_2+NH_4-oxalate, and samples treated with H_2O_2+NH_4-oxalate+Na-dithionite-citrate-bicarbonate.

The obtained results showed that kaolinites (kaolinites which form intercalation compounds with DMSO-Kl$_D$ and kaolinites which do not intercalate with DMSO-Kl) (RANGE et al., 1969), illitic material (ŚRODOŃ, 1984; ŚRODOŃ & EBERL, 1984), and Fe-oxides are the main mineral components in the clay fraction of the terra rossa. Calcocambisol enriched in organic matter contains kaolinites, chlorite and vermiculite as main mineral phases. The main differences in surface properties between the Terra rossa and Calcocambisol were a consequence of diverse particle-size distribution, mineral composition, and the share of organic matter. FE-SEM analysis of the Terra rossa and Calcocambisol samples after removal of amorphous Fe-oxides and organic matter shows disintegration. This disintegration is evident in reducing particle size from 2 µm to 50 nm for the Terra rossa and from 1.8 µm to 50 nm for Calcocambisol, respectively. Kaolinite with particle size about 50 nm shows pseudohexagonal form in analysed soils. The SSA increased proportionally to the amount of the removed organic matter in both soils. After the removal of well-crystallized Fe-oxides the SSA slightly decreased in Calcocambisol and significantly increased in the Terra rossa due to major soil microaggregate decomposition. EPM measurements of investigated samples were diverse.

Acknowledgments
This study was financed by Croatian Science Foundation (grant 2504).

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Mg–Fe LDH derived from magnesite and hematite and its affinity towards sulphates

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With an increasing demand for natural and relatively cheap materials for water purification, modified clay minerals are gaining more attention because of their effectiveness in anions removal (BEALL, 2003). However layered double hydroxides (LDH), called also "anionic clays" due to their similarities to clays, are synthetic and widely used materials with high affinity towards anionic forms (CHUBAR et al., 2017). Both clays and LDH have layered structure and variable layer charge, as well as similar colloidal and rheological properties. LDH with their general formula $[M^{II}_{1-x} M^{III}_{x} OH_2]_x$+$[A^{n-}]_{x/n}$×$yH_2O$ are synthetic forms of natural minerals called hydrotalcites. They are built of positively charged brucite–like layers and hydrated anions between the layers which balance the charge. The LDH synthesis in laboratory conditions is very easy, but the need for using chemical reagents makes the whole process expensive. Therefore, the aim of this study was to use minerals as sources of trivalent and divalent metals to synthesize Mg–Fe LDH as well as their calcined analogues. Moreover, the investigation on their affinity towards sulphates (SO_4^{2-}) was carried out.

For the synthesis, magnesite [M], hematite [H], $MgCl_2 \times 6H_2O$ [Mg] and $FeCl_3 \times 6H_2O$ [Fe] were used as sources of magnesium and iron in order to obtain Mg-Fe LDH. Materials were obtained in different combinations: Mg – Fe, M – Fe, Mg – H, M – H. Magnesite and hematite were dissolved in hydrochloric acid before the synthesis to obtain Mg^{2+} and Fe^{3+} chloric solutions. The pH of Mg^{2+} solution was set to 10 by an aqueous NaOH, then the solution containing Fe^{3+} was added dropwise to the solution of Mg^{2+} with constant pH control in the range of 9–10. Solution was aged for 2 h at room temperature, washed with redistilled water and dried at 60˚C overnight. Materials were calcined at 400˚C for 3 h. The obtained materials were characterized by XRD, FTIR and SEM.

The XRD patterns confirmed the presence of LDH in all samples, as compared to magnesium iron carbonate hydroxide standard pattern (JCPDS #14-0293) (FAHAMI & BEALL, 2016). Simultaneously brucite (JCPDS #44-1482) was formed in all samples excluding the M – H sample. This was also confirmed by FTIR (band at 3700 cm^{-1}) (MILLIS et al., 2012). Moreover, characteristic vibrational bands of CO_3^{2-}, Mg-O and Fe-O were observed. The SEM images of obtained materials, compared to the starting mineral substrates, clearly indicated the changes of morphology. Tabular particles with characteristic for LDH layered structure were observed.

The obtained materials were tested in SO_4^{2-} sorption experiments using aqueous solution of K_2SO_4 with concentrations set to 1.0 mM/L and 5.0 mM/L and initial pH = 5. The SO_4^{2-} concentration was determined using turbidimetric method with $BaCl_2$. The sorption capacity measured for the 5 mM/L concentration did not exceed 130 mM/kg for the uncalcined materials. However, the sorption capacity measured for the calcined materials was not lower than 180 mM/kg and did not exceed 210 mM/kg. Thus, it is worth to notice, that the structure reconstruction of the calcined LDH increased the sorption capacity of the investigated materials. The mechanism responsible for the anion uptake by the uncalcined LDH was an anion exchange. Both mechanisms were confirmed by XRD and FTIR.

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Structural transformation of lepidocrocite-type layered titanate, $Cs_{0.8}Ti_{1.6}Ni_{0.4}O_4$, *via* acid treatment and subsequent calcination at different temperatures

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Due to semiconducting property and intercalation ability, lepidocrocite-type layered titanates, whose general formula is $A_xTiM_yO_4$ (A; interlayer cation, M; vacancy or metal) (Fig. 1), have been utilized extensively as precursors for designing functional materials such as photocatalyst or lithium ion battery anodes (OGAWA et al., 2014). It is known that lepidocrocite-type layered titanate whose Ti ions are partially replaced with vacancy transforms into titania (TiO_2) *via* extraction of interlayer alkali metal cation and subsequent heat treatment. This phenomenon is likely to be ascribable to the fact that the chemical formula and local structure of the nanosheet is similar to that of titania (YUAN et al., 2014). On the other hand, the formation of metal-doped titania or metal oxide/titania composite can be expected by using lepidocrocite-type layered titanate whose Ti ions are partially replaced with metal ions as a starting material. In this study, lepidocrocite-type layered titanate, $Cs_{0.8}Ti_{1.6}Ni_{0.4}O_4$, prepared by solid-state reaction according to the previous report (GAO et al., 2009) was reacted with dilute HCl to extract the interlayer cesium ion, and then calcined at different temperatures in air.

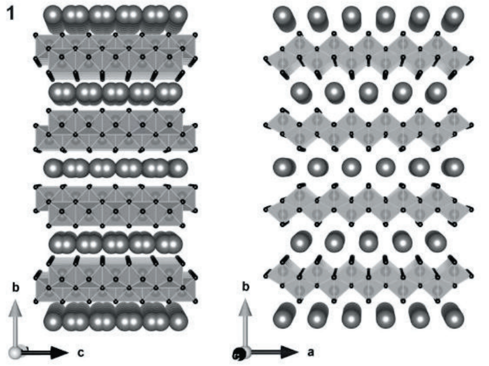

Figure 1. The crystal structure of lepidocrocite - type layered titanate.

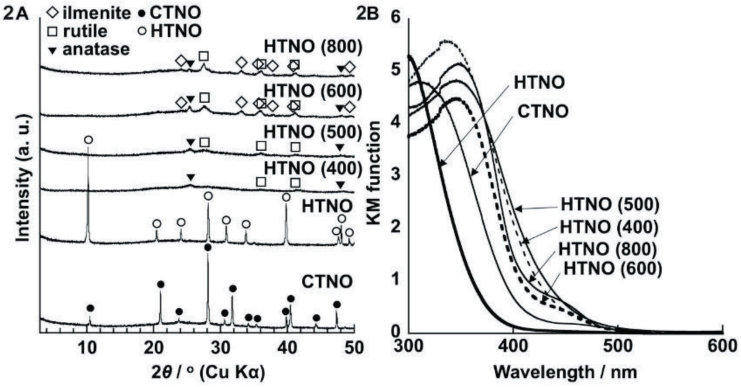

Figure 2. (A) XRD patterns and (B) diffused-reflectance UV-vis spectra of the products.

Figure 2A. shows X-ray diffraction (XRD) patterns of the products. All the diffraction lines of the product prepared by solid state reaction were assigned to those of $Cs_{0.8}Ti_{1.6}Ni_{0.4}O_4$ (the product is referred to as CTNO hereafter). The d (020) value of CTNO increased from 0.84 nm to 0.87 nm via HCl treatment, indicating that cesium ion was exchanged with hydrated proton to expand interlayer space. The protonated layered titanate before and after calcination are termed HTNO and HTNO (X) (X represents calcination temperature), respectively. While HTNO (400) and HTNO (500) were dual phase of anatase and rutile, formation of ilmenite ($NiTiO_3$) in addition to anatase and rutile was confirmed for HTNO (600) and HTNO (800).

Figure 2B. shows diffused-reflectance UV-vis spectra of the products. Titania is known to absorb light with wavelength shorter than ca. 410 nm, which corresponds to their band gap energy. Red shift of light absorption edge observed for HTNO (400) and HTNO (500) is likely to be ascribable to the fact that Ni ion was doped into titania phase to create a localized state in the band gap. This result is in good agreement with the fact that no diffraction lines attributable to Ni compounds were observed in the XRD patterns of HTNO (400) and HTNO (500). Light absorption edge of titania in HTNO (600) and HTNO (800) was very similar to that of undoped titania, indicating that Ni ion was completely removed from titania to form ilmenite. Possible charge transfer between titania and ilmenite in the products will also be discussed in the presentation based on their photocatalytic activity.

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Characterization of Tagaran natural clays and its use as adsorbent for removal of a model cationic dye

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A clay sample from Tagaran (TC) located in the Kurdistan region of Iraq-Sulaimani was used to investigate the adsorption of cationic dye (Methylene Blue (MB)) from aqueous solutions. The clay was characterized by XRD, XRF, SEM, FT-IR, and TG. It is dominated by a trioctahedral smectite with minor amounts of chlorite. Adsorption tests were conducted batch wise and effects of pH, equilibrium time and temperature, clay dosage, and MB concentration on adsorption efficiency were studied. The equilibrium data were fitted to the Freundlich, Langmuir and Temkin isotherms by linear and non-linear methods (KUMAR et al., 2008). The best-fit equations of linear and non-linear forms of the two widely used kinetic models, namely pseudo-first-order and pseudo-second-order equations were compared in this study (KUMAR, 2006). In addition, the activation energy and both calculated and experimental adsorption capacity are close to each other, too. It is concluded that natural clay may be locally used as an adsorbent for removing MB from wastewaters.

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Development of special clay blends for fibre reinforced plasterboards to improve fire resistance

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Plasterboards are not suitable as construction material for fire protection, without additives. This is primarily due to the very high shrinkage of the boards in case of fire, along with the dehydration of gypsum. As a consequence, the surface shrinks by more than 20 %, the boards burst from the screwed connections, so that there is no barrier effect any longer.

In order to render plasterboards suitable for fire protection, they are usually reinforced with special glass fibres. However, this improvement will be sufficient only if unpurified natural gypsum is used as raw material for the hemihydrates. In contrast, if pure synthetic gypsum is used, the sole addition of glass fibres will not yield the desired results.

In the framework of this study, dilatometric tests using different clay types such as bentonites, china clay, loam and different plastic kaolinitic clays, were carried out to evaluate the shrinking behaviour of hardened gypsum slurry specimens mixed with glass fibres and different clay types. Figure 1. shows the shrinkage performance of a final optimized product in comparison with an ordinary heavy clay and the shrinkage of the cast gypsum sample without clay additives.

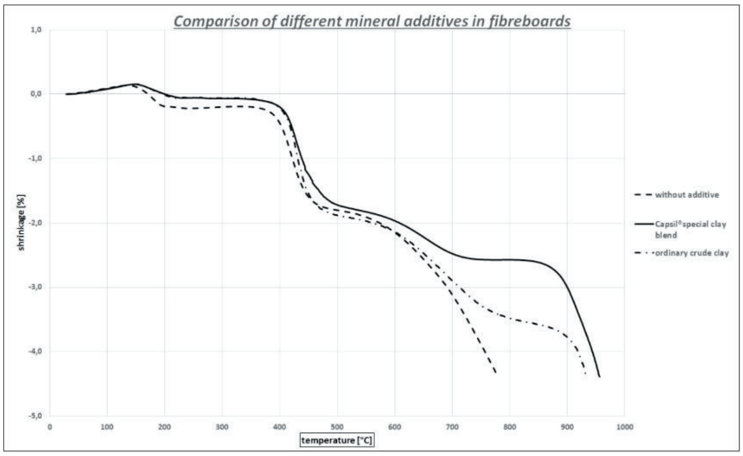

Figure 1. Dilatometry curves of Capsil® Special Clay vs. ordinary crude clay.

Further examples are shown in the complete study (SCHELLHORN & DIEDEL, 2017). In conclusion, the dilatometry test is an easy and reliable test for the development of fire resistant plasterboards.

Other parameters such as flow spread, drying behaviour and screwing behaviour of the boards have also been taken into consideration within the scope of this study.

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Molecular mechanism of dissolution, growth and ion incorporation of clay minerals at the mineral/water interface

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Due to their high sorption capacity, clay minerals and clay rich rocks are widely used as backfill material in disposal sites to protect the environment from toxic waste, heavy metal contaminants and radionuclides. The interplay between adsorption and desorption, crystal growth and dissolution and changes in pore water chemistry is of key importance for the prediction of the pollutants transport and retention in geochemical environment over time. Atomistic simulations can help to obtain a deeper understanding of the underlying mechanisms and their respective time scales. Several aspects of the uptake processes have been investigated. Nevertheless, a complete and consistent description of those has not been achieved yet, especially when it comes to the uptake of surface complexing ions. While the exchange reaction of interlayer cations or the adsorption at the basal planes is well understood (ROTENBERG et al., 2009) and can be related to hydration energy of the cation, the sorption process on the edge sites is on the other hand quite complex (CHURAKOV & DAEHN, 2012). The latter is known to be pH dependent, which results from different protonation states of the surface oxygen sites that change the surface affinity towards adsorbed ions. Furthermore, the dissolution and growth of clay platelets at the edge sites most likely modify the surface topography and the availability of sorption sites (KURGANSKAYA & LUTTGE, 2013). These processes are responsible for a durable entrapment of contaminants since they involve direct structural incorporation of hazardous ions.

In this study, we investigate the molecular mechanism of clay mineral dissolution at edge sites by ab initio molecular dynamics simulations based on density functional theory. We use the Metadynamics (MtD) approach (LAIO & PARRINELLO, 2002) to obtain activation energies for subsequent detachment of mineral building tetrahedral and octahedral ions at the edge sites. Initial simulations are performed for pyrophyllite which represents a reference model for an uncharged phyllosilicate (TOT structure type). The most stable (110) edge surface was studied first. The system size and the amount of water between the edge surfaces was chosen to minimize the interaction between opposite surfaces and to maintain the water density in the middle of the water slit pore close to 1 g/cm^3. Coordination numbers for different atomic pairs were used as collective variables (CV) for the MtD.

The preliminary simulation results in pH neutral water show that dissolution of the silicon tetrahedron, forming a structural step at the edge, is going through at least three steps by breaking all three oxygen bridges to neighbouring Si-tetrahedrons (Si(t)) and one Al-octahedron (Al(o)). Plotting the free energy surface with CVs as coordinates shows a global minimum that is the initial state and local minima corresponding to the dissolution steps. Activation energies were obtained through the minimum energy pathways between these two types of minima. The information regarding the mechanisms and energies has extreme importance for the parametrisation of the kinetic Monte Carlo (KMC) models of dissolution, growth and surface adsorption. Based on the previous KMC approach (KURGANSKAYA & LUTTGE, 2013), we are developing a model of montmorillonite particle dissolution and growth as a function of saturation state. In this study, we demonstrate the influence of the activation energies for Mg-O-Si and Al-O-Si bond breaking on the step edge morphology. The corresponding parameter sensitivity study will be further followed by a new ab-initio based parameterization approach, where the above mentioned molecular models incorporating interface water structure and lattice size influence are adopted.

Acknowledgements
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Laponite® technology: present status, challenges and future trends

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Over the last five decades, Laponite® materials have become a customary presence in a variety of technological applications as well as the focus of extensive scientific research. Already great and constantly growing number of patents, research articles and reviews is a testament of the enduring legacy of this family of synthetic clays in industry and academia.

What makes these materials so special to allow such a sustained following to occur? Is it high purity and consistency of Laponite® grades throughout many years? Is it an unusual combination of super-fine size, precisely defined charge and other individual platelet characteristics, that enable a spectrum of unique Laponite® properties and physicochemical behaviours? Is it the technological advantages of Laponite®, including extremely fast dispersion in water, powerful gelation, and easy combination with other materials such as polymers, organic molecules, and inorganic solids to produce potent synergistic effects? Is it the ability of Laponite® to form Pickering emulsions, stabilising oil droplets in water and vice versa? Perhaps, the most obvious answer is – all of the above.

In this presentation, we would like to remind the expert community of the history of Laponite® technology, starting with its discovery by Dr. Barbara S. Neumann (NEUMANN, 1962; NEUMANN, 1966; NEUMANN, 1972; TAYLOR & NEUMANN, 1968; NEUMANN & SANSOM, 1970) of the then Laporte Industries, discuss some of the key properties of these materials and briefly review the most established technological applications.

In addition, we are going to share some of the challenges in the analysis of the Laponite® family of synthetic clays. These challenges involve robust and statistically correct measurements of individual platelet sizes; finding appropriate methods for establishing charge-related characteristics of Laponite; implementing novel and more insightful techniques for testing dispersibility and gelation of Laponite® clays, for instance, in aqueous medium, and so on.

We shall give some examples of tackling the challenges outlined above, in a hope to initiate fruitful discussions and gain expert insights into these problems.

Finally, we shall aim to present a brief overview of the current and future trends in Laponite® applications with particular emphasis on recent developments in the biomedical field (FRAILE et al., 2016; GONCALVES et. al., 2014; TOMAS et. al., 2017) and other, higher-end industrial uses of these materials (LI et. al., 2014; MISHRA et. al., 2012; MUSTAFA et. al., 2016).

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The nature, origin and significance of luminescent layers in the Bazhenov Shale Formation of West Siberia, Russia

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Argillites that strongly luminesce under UV radiation were detected in the Bazhenov Shale Formation (BSF) of the West Siberian Basin during routine core examination and found to be persistent over an area of more than 500 km wide. The Bazhenov Formation was formed during the Late Jurassic time and represents the main source rock in the West Siberia petroliferous basin (SHALDYBIN et al., 2017).

The mineralogy and fabric of these luminescent layers were characterized by optical and fluorescence microscopy, SEM, TEM, XRD and IR methods for 6 samples. Optical and fluorescence microscopy showed that the luminescent layers were to a large extent derived from volcanic ash falls and could be described as tuffaceous rock, although normal detrital sedimentation continued at the same time. The layers are clay-rich and XRD showed that two principal clay minerals are present, namely a well-crystallized kaolinite with significant (possibly major) dickite stacking and a felted network of mixed-layer illite-smectite (I-S) stacked in a regular arrangement. Total organic matter content in the luminescent layers is much lower than that in the enclosing BSF clayey-silty siliceous sediments above and below as shown by pyrolytic analyses using Rock-Eval. Evidence is presented that the luminescent characteristic of the argillites is related to their clay mineralogy, specifically to their highly ordered kaolin mineral content. In some way the luminescent argillites can be compared with tonsteins in coal beds, which are also derived from volcanic ash falls and contain highly ordered kaolinite (SPEARS, 2012).

However, tonsteins originate at or near land surface whereas the thin-laminated argillites of the Bazhenov Shale were apparently formed in a deep-sea basin. But just as tonsteins can be used for detailed stratigraphic studies and are valuable in the context of coal exploration, so may the luminescent argillites prove to be significant as stratigraphic markers for the West Siberia basin.

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Application of high gradient magnetic separation for characterization of glauconite weathering products formed in soils under different pH conditions

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The aim of the present research was to compare products of glauconite weathering occurring in two soils formed under temperate climate having different pH. According to SKIBA et al. (2014), who studied weathering in acidic soil developed on quartz-glauconite sand in Góra Puławska (eastern Poland), glauconite weathered into smectite-rich glauconite-smectite mixed-layered minerals. Formation of kaolinite at the expense of glauconite was also suggested (SKIBA et al., 2014). Recent studies of alkaline soil developed on calcite-bearing quartz-glauconite sand in Górniki (eastern Poland) also indicated that smectite-rich glauconite-smectite minerals were the main products of glauconite weathering. Formation of kaolinite was also indicated by the fact that kaolinite was identified not only in clay fraction of the soil but also in glauconite pellets separated from upper horizons. Small concentration of goethite was identified among the products of glauconite weathering and the presence of XRD-amorphous iron phases was suggested (unpublished data).

For better characterization of the weathering products from the two profiles high-gradient magnetic separation was applied to concentrate minerals having different magnetic susceptibility. The Frantz LB-1 Magnetic Barrier Laboratory Separator was used. Na-saturated clay fractions from C and B soil horizons from each profile were dispersed in deionized water and passed through the canister filled with steel wool and placed in the magnetic field induced by electric current of 1.6 A. Separated magnetic and non-magnetic subfractions were analyzed using XRD.

Magnetic fractions from both soil profiles were dominated by glauconite. 10 Å phase was also detected in nonmagnetic fractions and it was especially abundant in nonmagnetic material from acidic soil. Smectite concentrated in nonmagnetic fractions, however, in magnetic fraction from alkaline soil it was also identified. 7 Å phase was detected in both magnetic and nonmagnetic fractions but it clearly concentrated in nonmagnetic fraction, especially in the material from alkaline soil. In magnetic fraction from alkaline soil goethite was detected, whereas magnetic fraction from acidic soil contained lepidocrocite.

Magnetic separation of clay material from the studied soils revealed certain differences between the two profiles, which may be due different pH conditions. The observed distribution of minerals between magnetic and nonmagnetic fractions may result from different chemical composition of minerals which influences their magnetic properties. The distribution can be, at least in part, affected by incomplete separation, although this effect should be minimized due to repeated separation of each sample. Natural aggregation of magnetic and nonmagnetic particles can be also the issue.

Acknowledgments

This study was financed by National Science Center of Poland (grant UMO-2016/23/B/ST10/02000).

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Structural analysis of beidellite and montmorillonite intercalated with acetylcholine and choline – computational investigation

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In the last two decades, organoclays intercalated with various organic cations were intensively studied combining theoretical and experimental methods. Two representatives of the smectite family (beidellite and montmorillonite) are widely used to prepare organoclays because of their excellent properties and various chemical interactions, such as high cation exchange capacity, swelling behavior, adsorption properties, large surface area, hydrogen bonds, ion–dipole interaction, and coordination bonds (EZQUERRO et al., 2015). Montmorillonite is commonly used as a nanofiller in the preparation of polymer nanocomposites. The surface energy of montmorillonite decreases and the basal spacing expands by exchanging sodium or calcium cations by organic cations (FAVRE & LAGALY, 1991). Beidellite is, for example, extensively used as an adsorbent for the removal of lead and cadmium ions from aqueous solutions (ETCI et al., 2008).

This work is focused on the experimental and theoretical study of organoclays based on beidellite (Bd) and montmorillonite (Mt) intercalated with acetylcholine (AC) and choline (C) in hydrated (hAC-Bd/Mt and hC-Bd/Mt) and dehydrated (dAC-Bd/Mt and dC-Bd/Mt) form, respectively (as example see Fig. 1). The models of the organoclays were studied by means of the density functional theory (DFT) method. DFT calculations were performed with dispersion corrections using a D3 scheme, which was taken as recommended for the PBE functional (GRIMME et al., 2010). The results from calculations were compared with available experimental data.

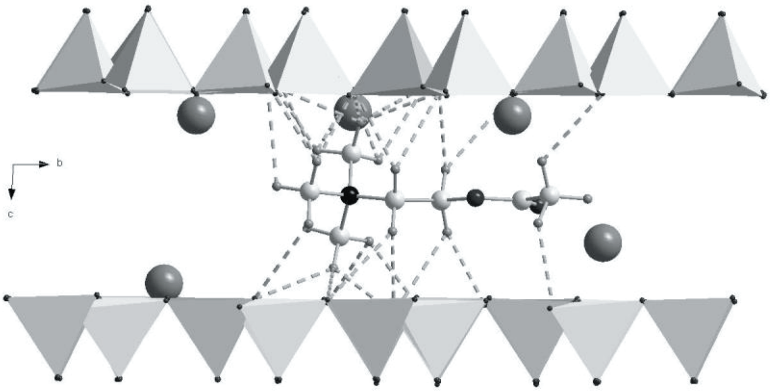

Figure 1. Model of structure of beidellite intercalated with acetylcholine. Hydrogen bonds are shown with dashed line.

Acknowledgments
This work was supported by the Slovak Research and Development Agency under the contract No. APVV-15-0741 and APVV-15-0347.

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The application of NIR spectroscopy for monitoring the conformation of a series of primary amines in montmorillonite interlayers

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Infrared (IR) spectroscopy is one of the most commonly used method for characterization of organoclays. Over the past decades, these inorganic/organic hybrid materials found application in a wide variety of industrial and scientific applications such as adsorbents of organic pollutants, pharmaceutical and cosmetic additives, reinforcing fillers for plastics, water treatment or host structures for direct intercalation of polymers. The behaviour and properties of organoclays strongly depend on the structure and arrangement of the intercalated surfactants, most often alkylammonium cations, in clay mineral interlayers. Detailed information on the arrangement of organic cations provides also near-infrared (NIR) spectroscopy.

The objective of this paper was to study the arrangement/conformation of the primary alkyl ammonium surfactants in the montmorillonite interlayers. The organo-montmorillonites were prepared from a Na-saturated <2 µm fraction of bentonite Jelšový Potok (JP, Slovakia) and alkylammonium (C_n-NH_3^+) salts with increasing length of alkyl chain from C5 to C19. The X-ray diffraction analysis was used to probe the arrangement of alkylammonium cations in the interlayers. The KBr pressed disk technique was applied for measurements in the middle-IR (MIR) region and diffused reflection (DRIFT) techniques was used for NIR.

The X-ray diffraction analysis showed basal spacing (d_{001}) in the range 1.35–1.95 nm (C5-JP – C19-JP) in dependence on the alkyl chain length. The basal spacing was almost the same (~1.33–1.37 nm) for montmorillonite saturated with C5 – C8 cations suggesting a monolayer arrangement. With further increase of the alkyl chain length the d_{001} values gradually increased from 1.41 nm (C9-JP) through 1.75 nm (C14-JP), 1.83 nm (C16-JP) to 1.95 nm (C19-JP), indicating consecutive transitions from monolayers to bilayers and pseudotrimolecular layer arrangement. The most pronounce increased of the d_{001} value was observed between C11 and C12 (~1.51–1.66 nm). The positions of the absorption bands related to the stretching vibrations (νCH_2) and the first overtone ($2\nu CH_2$) of the methylene groups were found to be very sensitive to the alkyl chain arrangements. The MIR spectra of organo-montmorillonites showed a gradual replacement of the asymmetric $\nu_{as}(CH_2)$ and symmetric $\nu_s(CH_2)$ stretching bands from 2934 to 2922 cm^{-1} and from 2862 to 2851 cm^{-1}, respectively. A gradual shift towards lower wavenumber with increasing alkyl chain length confirmed a transition from disordered (*gauche*) to more ordered (all-*trans*) conformers of the surfactants. The NIR spectra of organo-montmorillonites showed a abroad complex band related $2\nu(CH)$ in the 6100–5600 cm^{-1} region and the combination ($\nu+\delta$) bands of CH_2 groups in the 4500–4000 cm^{-1} region. The positions of the $2\nu_{as}(CH_2)$ (~5830–5786 cm^{-1}), $(\nu+\delta)_{as}CH_2$ (~4362–4330 cm^{-1}), $(\nu+\delta)_sCH_2$ (~4276–4255 cm^{-1}) signals were used as an indicator of the *gauche*/*trans* conformer ratio. For all bands a shift towards lower wavenumber with increasing the alkyl chain length suggested a transition from disordered liquid-like to more ordered solid-like structures of the surfactants. The most significant shift of the bands was observed between samples C10 and C11 (10 cm^{-1}), indicating critical point of length dependent conformational change. The magnitude of the overall shift of $2\nu_{as}CH_2$ (46 cm^{-1}) was significantly higher than those observed for $\nu_{as}CH_2$ (12 cm^{-1}) or ν_sCH_2 (11 cm^{-1}), showing the NIR spectroscopy to be very suitable for studying the conformation of surfactants in organo-clays.

Acknowledgments
The financial support of the Slovak Research and Development Agency (APVV-15-0741 and APVV-15-0347) and the Slovak Grant Agency VEGA (2/0141/17) is gratefully acknowledged.

Thermal history of the central part of the Karst Dinarides, Croatia: combined application of clay mineralogy and low-T thermochronology

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This study was undertaken to unravel the thermal history (values, timing, and origin of the maximum palaeotemperatures, rates of exhumation) of the central part of the Karst Dinarides, exposed along the NE Adriatic coast in the Velebit Mt. and neighbouring areas. An additional research objective was tracing the behaviour of haematite crystals during diagenesis. The lower, partly clastic part of the sedimentary section (Upper Carboniferous and Permian mudstones, Triassic mudstones and pyroclastics), covered by a thick succession of Mesozoic carbonates has been studied by a combination of mineralogical techniques (XRD+SEM), K–Ar dating of illite, apatite fission track (AFT), as well as apatite and zircon (U–Th)/He thermochronology.

The commonly occurring minerals, detected by XRD, are quartz, albite, K-feldspar, illite, mixed-layer illite–smectite, chlorite, kaolinite, calcite, dolomite, pyrite, hematite, and goethite. A few samples contain vermiculite, paragonite, siderite, jarosite, gypsum, boehmite, and marcasite. Illite plus illite-smectite dominate: 25-90 wt%. Illite-smectites contain up to 30 % of smectitic layers. In pyroclastic rocks 1M polytype and partly aluminoceladonitic composition are common. Paragonite occurs as minor component along with $2M_1$ illite and rarely with sudoite. Boehmite was identified along with kaolinite, calcite and hematite in a bauxite layer. Vermiculite and swelling chlorite were considered as products of contemporary outcrop weathering following ŚRODOŃ et al. (2013) and MARYNOWSKI et al. (2017). Clay minerals were used to evaluate the maximum paleotemperatures.

A consistent model of the thermal history of the study area was obtained. The Carboniferous to Triassic sequences NW of the Split–Karlovac fault experienced maximum burial temperatures between >200 and 270°C, while lower palaeotemperatures (ca. 150°C) were detected in the Middle Triassic rocks to the SE of the fault. The maximum palaeotemperatures were recorded earlier (during the Late Cretaceous–Palaeocene) than expected during the period of maximum sedimentary and/or tectonic burial in Mid-Eocene and Early Oligocene, corresponding to the major thrusting phase in the studied part of the Dinarides. Rapid exhumation started in the studied structural domains between 80 and 35 Ma, i.e. between the Campanian and the end of Eocene, followed in some domains by a younger exhumation and cooling pulse.

Hematite, the main carrier of the palaeomagnetic signal in the studied area, was shown to recrystallize at temperatures above 120°C, which explains the appearance of secondary magnetization well below the Curie point of hematite, such as reported recently in the Central Velebit Mt. area.

Acknowledgments
This study was mostly funded by the project no. N307 475238 granted to Marek Lewandowski by the Polish Ministry of Science and Higher Education, and in part by the Croatian Science Foundation project IP-2014-09-9666. We thank Marta Mileusnić for her help during the field work.

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Computational modelling of the interactions of kaolinite with heavy oil components in solution

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The oil sands of Western Canada hold the third largest hydrocarbon deposit in the world. Oil sand is a composite of bitumen, mineral solids, and water, from which the bitumen is recovered either by warm-water extraction of mined ore, or by various *in situ* methods. Bitumen froth produced using the surface mining process is treated with light solvent to separate fines and water from bitumen product. Bitumen, a very heavy petroleum, contains large amounts of asphaltenes that have a tendency to aggregate through supramolecular assembly interactions. The oil sands solids contain mostly silica with substantial amounts of clay particles, mainly kaolinite and illite. Kaolinite, the most abundant oil sands clay mineral, has hydrophobic and hydrophilic surfaces that interact with bitumen, posing major challenges to hydrocarbon recovery and environmental remediation of aqueous tailings. Non-aqueous extraction, a possible alternative to the water-based extraction process for mined ore, might operate at mild conditions and eliminate water use, but faces challenges related to asphaltene extraction and solvent recovery (LIN et al., 2017).

Multiscale computational modelling has been employed to study the interactions of kaolinite with model compounds representative of petroleum components in order to address important aspects of non-aqueous extraction of bitumen from oil sands. In this multiscale modelling approach, solvation effects are calculated using the 3D reference interaction site model with the Kovalenko-Hirata closure (3D-RISM-KH) (KOVALENKO, 2003). The 3D-RISM-KH method yields the solvation free energy of a solute and predicts correctly the kinetic and surface adsorption energy barriers that have to be overcome by molecules approaching a solvated solid surface. The electrostatic and dispersion interactions between solute components are calculated using electronic structure methods or force fields (LAGE et al., 2018).

The computational studies reveal complex multipoint molecular recognition interactions that govern the adsorption of heterocyclic model compounds, representing asphaltenes, on kaolinite in hydrocarbon solvents (HUANG et al., 2014). Multilayer adsorption is correlated with experimental adsorption isotherms, highlighting the capability of 3D-RISM-KH to account for the effects of aliphatic and aromatic solvents on the adsorption of aromatic amine model compounds on kaolinite (HUANG et al., 2014). The thermodynamics and kinetics of interaction of extraction solvents with kaolinite are studied to understand the mechanism solvent retention in tailings (STOYANOV et al., 2018). An advanced approach for non-aqueous extraction based on the use of polar co-solvents is also investigated (LAGE et al., 2018). The computational results are presented in comparison with experimental adsorption measurements.

The results present a detailed mechanistic picture of the kaolinite-heterocycle interactions in solution obtained using the powerful multiscale modelling platform we have implemented. The modelling insights are aimed to help understand these molecule-surface interactions in a range of thermodynamic conditions of solvation and provide recommendations for addressing challenges in the recovery of bitumen from oil sands.

Acknowledgments

This study was supported by the Government of Canada's interdepartmental Program of Energy Research and Development (PERD), as part of the project Review of Technology Status and Retention of Diluted Bitumen in Solids.

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Competitive adsorption of Cs and Sr onto raw and amphoteric surfactant-modified Laponites®

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Clay minerals are widely considered as suitable materials for the long-time storage of radionuclides (MONTOYA et al., 2018). However, few works have been interested in the removal of radionuclides from contaminated effluents by clays and modified clay materials (ABDEL RAHMAN et al., 2011). Currently, the production of effluents contaminated by radionuclides is mostly derived from nuclear energy production. The aim of this work is to develop a new adsorbent able to remove these contaminants before a long-time storage. In this context, raw clay materials present several weaknesses for the adsorption of some radionuclides, such as Sr and Cs.

Laponite®, a commercial patented material, was used as raw material in this work. This study emphasizes the modification of the clay mineral by the intercalation of an amphoteric surfactant within its interlayer space. This work reports the preparation and characterization of the raw and synthetized adsorbents by several technics, such as XRD, FTIR, ^{29}Si and ^{1}H NMR, in order to precisely determine their structures.

Kinetic and isotherm adsorption tests were conducted in order to determine the adsorption capacities of Sr(II) and Cs(I) alone or in competition onto the different adsorbents. The concentrations of each radionuclide ranged from 1 to 1000 µM. Langmuir, Freundlich and Dubinin-Radushkevich adsorption models were fitted to experimental data in order to determine the thermodynamic parameters of adsorption. After adsorption, desorption experiments have been conducted in different saline solutions, in order to characterize the reversibility of adsorption.

It was shown that Sr(II) was adsorbed through cation exchange onto the different adsorbents, the highest adsorption capacity was noticed onto Laponite®. The adsorption of Cs(I) was weak onto the raw clay mineral, whereas the adsorption capacity onto hybrid material was improved. These trends were observed both for the adsorption of each radionuclide alone or in competition. The adsorption capacities in competition were systematically lower than that of each radionuclide alone. Each adsorbent exhibits different performances for the adsorption of individual radionuclides, however it is difficult to discriminate one adsorbent which would perform better than the others based on adsorption experiments.

The type of interactions was inferred by the models. Weak interactions (i.e. physisorption) have been modelled for Cs(I) adsorption onto raw material, whereas the others look like strong interactions (i.e. chemisorption and/or complexation) ensuring high and stable adsorption capacities.

Desorption experiments of Cs(I) and Sr(II) were performed in order to check the stability of the adsorbates. Cs(I) was mostly released (from 40 to 70 %) in every tested saline solution. However, the release was higher in Na(I) solution rather than in Ca(II) and pure water solutions. The divalent Sr(II) was in the same way more released in Ca(II) solutions in comparison with Na(I) and pure water, but the released percentage is lower (i.e. 1 to 30 %) than that of Cs(I).

With these results, it can be considered that the new modified clay is a good candidate for the decontamination of liquid effluents containing radionuclides. Studies are underway to improve the capacity of the new functionalised media.

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Effect of calcined bentonite as a supplementary cementitious material on the long-term performance of concrete

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The objective of using supplementary cementitious materials (SCMs) in cement is to reduce costs and the overall CO_2 output of the cement production. Against the increasing demand for cement and the decreasing availability of common SCMs, calcined clays serve as alternative materials for the industrial-scale manufacture of composite cements. In the present study, a raw clay of high volume capacity was selected to check its pozzolanic activity after suitable thermal treatment and the consequent effects on the concrete performance. The results show that, at high cement substitution rates of 30 %, the properties of the concrete remain unchanged to a significant extent (Fig. 1). In certain durability issues namely sulphate resistance, inhibition of alkali silica reaction (ASR) and chloride migration, the mixture with calcined clay performed better than the reference. Other properties like final strength and frost and de-icing salt resistance were changed only within the specification limits of a standard cement. Negative effects have been observed on the early strengths and on the carbonation velocity. However, giving careful consideration to these aspects while concrete projecting, the calcined clay is a suitable material for the vast majority of concrete applications. Consequently, the studied material as well as similar activated clays are proved to be high quality SCMs and, hereby, provide potential to replace Portland cement together with the related costs and CO_2 emissions of production.

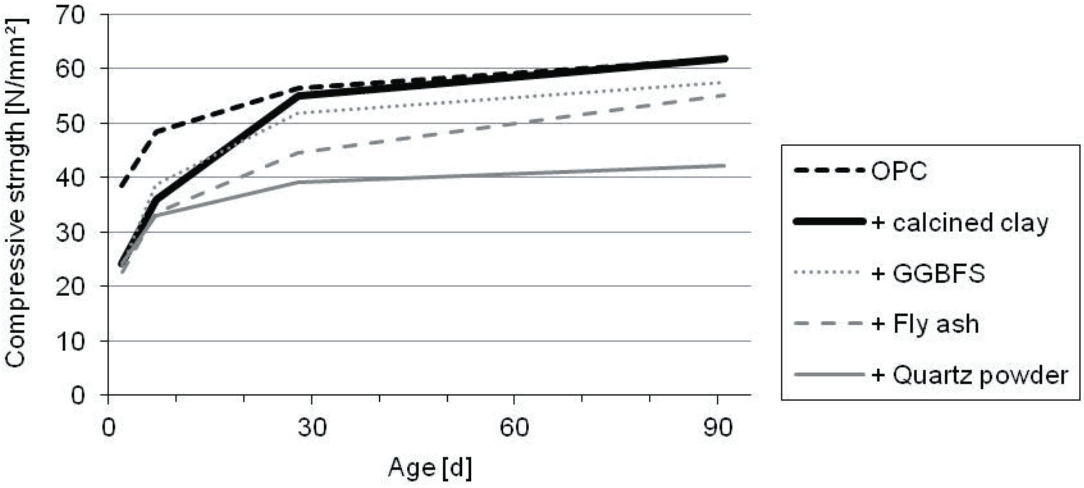

Figure 1. Strength development of the calcined clay blended cement (30 wt% substitution) compared to different reference systems (OPC: portland cement; GGBFS: slag sand).

Acknowledgements
The present study was funded by the Federal Ministry for Economic Affairs and Energy based on the orders of the German Bundestag. The authors like to express their special thanks to that support.

The combination of different disorder models for the Rietveld refinement of rectorite, a regular interstratified clay mineral

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The clay mineral rectorite is a regular interstratification of dioctahedral mica (illite, I) with dioctahedral smectite (S), which occurs in hydrothermal veins, in altered bentonites or as an alteration product of muscovite during shale diagenesis. Statistically it can be described as a Reichweite 1 ordered interstratification with 50 % of each component and a probability of two neighbouring layers of the same kind equal to zero. In other words, rectorite shows a perfect sequence of ISISIS… . X-ray diffraction patterns of oriented mounts in the air-dried state show a rational series of basal reflections with a repeating distance of 22.5 Å to 25 Å, depending on the interlayer cation and the relative humidity. In the ethylene glycol intercalated state, the repeating distance is 27 Å. These repeating distances can be interpreted as the sum of the layer thicknesses of the two components illite and smectite. Small deviations from perfect rationality are accepted to distinguish rectorite from other illite-smectite interstratifications. This deviation is expressed by the coefficient of variation (CV), which describes the regularity of alternation of an interstratification. The CV is below 0.75 for rectorites. Another possibility to characterize an interstratification is the application of the Rietveld method, as demonstrated by UFER et al. (2012a). This allows the description of an interstratification in terms of the proportions of components and junction probabilities.

In contrast to the high rationality of the basal reflections, the non-basal reflections of random powder patterns show strong intensity modulations which cannot be interpreted as Bragg peaks. This indicates the presence of rotational or translational disorder of the layers parallel to each other. These disorder effects can be random like the turbostratic disorder common in smectites or the rotations are multiples of 60° or 120° like in disordered illites.

It will be demonstrated that existing disorder models for interstratifications, rotational disorder (UFER et al., 2012b) and turbostratic disorder (UFER et al., 2004) can be combined to describe rectorites. Reference samples will be characterized by this approach and the results will be compared to additional analytical data (DIETEL et al., 2015).

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Mineralogical characterisation of Batizovské pleso sediments (High Tatras, Slovakia)

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The High Tatras (HT) moraine relief shows a glacier stabilization in two phases, at 26–21 ka and at 18 ka (MAKOS et al., 2014), followed by a gradual retreat and formation of the morainic, trough and cirque lakes dated from 10000 to 16000 cal BP on the northern slopes of the Tatra Mountains and before 10000 cal BP on its southern slopes (KLAPYTA et al., 2016). Sedimentary record of HT mountain lakes contains two distinct lithostratigraphic sections. The uppermost part is formed of the Holocene brown detrital gyttja with high organic matter content which overlays the Late Glacial mineral light-grey silt and fine-sand which suggest deposition under dry and cold periglacial conditions (KLAPYTA et al., 2016).

The contribution intends to present the first results of the mineralogical analysis of the tarn sediments on the Slovak side of the High Tatras and belonging to complex paleolimnological study of High Tatras tarns with aim to determine a timing of the glacier disappearance and amplitude of climatic and ecological changes on the glacial/interglacial boundary (http://www.geo.sav.sk/en/depovyt-apvv-15-0292/).

Batizovské pleso (1884 m a.s.l) is a mountain lake (tarn) formed by a glacier. Its sedimentary record have been obtained by using a swimming platform. Drilling site was selected after a lake sonar survey, which provided high resolution 2D acoustic image on sedimentary infill. This allowed a selection of the site with the highest thickness of the sediment. Drilling was realized by steel hydraulic corer allowing to get 2 m long core. Total thickness of lake sediments was more than 3 m. Non-destructive micro-CT analysis was used to determine the internal structure of the sediment in the cores before cutting. The cores were devided to 1 cm thick samples. Part of these samples were analysed by particle size and XRD analysis (bulk and clay fraction).

Upper part of Batizovské pleso sediments is composed by gyttja (postglacial sediment with organic matter). Dominant particle size of this sediment is fraction less than 0.063 mm. 40–80 wt% of amorphous phase was determined in gyttja by XRD. The rest is composed by same minerals as were identified in-light grey laminated glacial silt. Analysed silt samples are composed of quartz, albite, K-feldspar, muscovite and clay minerals: illite, smectite, chlorite and kaolinite. Most of this mineral assemblage corresponds to the surrounding rocks (mainly biotite tonalites and granodiorites; NEMČOK et al., 1993). Amount of clay minerals varies from 5 to 25 wt% and is independent on depth. Quantitative changes of mineral composition are explained by different dynamics of sedimentation. XRD analysis of clay fraction confirmed presence of illite, chlorite, kaolinite and smectite. While representation of the first three clay minerals in the studied clay fraction of light grey laminated silt is practically unchanged, amount of smectite is variable, from traces to major phase. Mineral composition of tarn sediments will be compared with mineral composition of surrounding soils.

Acknowledgments
This work was supported by the grant APVV-15-0292.

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Synthesis of dioctahedral clay minerals under low temperature hydrothermal conditions for different time periods

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Smectite and kaolinite are clay minerals widely distributed in the Earth's crust. Both clay minerals are also used largely for various applications in many fields. However, the crystal growth process of these clay minerals is still poorly known. The synthesis approach potentially allows to control the crystallisation of clay minerals and notably to manage the time parameter.

In this study, the synthetic samples were crystallized from gels under hydrothermal conditions. Gels were prepared by sodium metasilicate ($SiNa_2O_3 \times 5H_2O$) and aluminum (III) chloride ($AlCl_3$) at 1:1 molar ratio. The pH of the gels was adjusted to 9.0 by 0.2 M NaOH. The syntheses were performed at 210ºC for 15, 20, 25, 30 days under equilibrium water pressure. The products were characterized by FTIR, XRD, TGA and SEM analysis.

XRD, FTIR and TGA data revealed that only part of the gel was reacted and that amorphous product remained at the end of synthesis whatever the ageing time. Depending of the ageing time, different clay minerals were synthesized. For the shortest durations (15 and 20 days), mixture of 2:1 clay mineral and kaolinite were revealed. For the 15 days experiment, the 2:1 did not swell under ethylene glycol (EG). For the 20 days experiment, the 2:1 clay mineral swelled partially after EG intercalation (from 10 Å to about 15 Å) and the amount of kaolinite was higher than for the 15 days experiment. For the 25 and 30 days experiments, kaolinite and a 2:1 unswelling clay minerals are observed as single phases respectively.

Acknowledgments
This study was financed by Mugla Sitki Kocman University with a grant number of BAP 17/011 project.

Stratigraphic distribution and lithofacial variations of Carboniferous shales

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The lithofacial and chemical characteristics of organic-rich Carboniferous mudstones were related to sequence stratigraphic units of a rifting basin. The composition of the analysed black shales reflects the conditions of sedimentation, post-rifting subsidence, water chemistry and thermal conditions of the Carboniferous succession (ULMISHEK et al., 1994). Examination area is the north-western part of the Dniepr-Donets Basin (Ukraine). The analyses of bore core samples from 12 wells provide an overview of the cyclic deposition of siliciclastic and carbonaceous sediments in fluvial, lagoonal and shallow-marine environments from the Devonian to the Serpukhovian period (SACHENHOFER et al., 2010). South-east of the Srebnen Depression the well Rud 2 allows a detailed stratigraphic analysis because of the sample density. The well intersects 1500 m of Upper Visean to Tournaisian layers of sandstone, shale and carbonate. 101 bore core samples of black shales originate from the productive horizons V-16 to T-5.

Qualitative and quantitative mineralogical analysis was carried out by X-ray diffraction analysis. X-ray fluorescence spectroscopy delivered the chemical data and served for the validation of the XRD-data. Leco and Rock Eval parameters provided information concerning the percentages of TOC, sulphur, calcite and thermal maturity data (SACHSENHOFER et al., 2012).

Within the productive horizons of the Upper Visean (V-16 to V-23), Lower Visean (V-24 to V-25) and Tournaisian (T-3 to T-5), the major mineralogical phases of the black shales are represented by kaolinite-group minerals, mica-group minerals and quartz. In minor quantities expandable clay minerals (primarily illite-smectite), chlorite-group minerals, feldspar, pyrite and siderite exist, whereby the increased values of Fe-sulfide and -carbonate in Upper Visean and Tournaisian occur. Different transport properties mainly caused the observed selective mineral concentration of illite and kaolinite.

The uppermost part of the Upper Visean succession can be distinguished by the occurrence of chlorite and a higher amount of diagenetic plagioclase. In the Upper Visean horizons V-19 and V-22 the increasing content of expandable clay minerals indicates post depositional heat flow. In horizons V-23 (Rudov Beds) and V-22 a maximum TOC content of up to 5 % occurs and can be related to three different sedimentation patterns of the main mineral phases kaolinite, quartz, illite, siderite and pyrite. In the Lower Visean carbonate contents up to 90 % indicate a major transgression. The upper part of the Tournaisian is characterized by carbonate-quartz-rich layers. In a depth of 5500 m the change of the sedimentation conditions are visible by a significant lithofacial change, represented by the high increase of the kaolinite content and after a further 100 m in a maximum content of siderite.

A correlation between the weight percentage of Si, K, Al and Fe and the main mineral phases could be observed. A weak correlation exists between the ratio of Zr/K plotted against quartz percentages. A further weak correlation was found between Ti and Al as well as TiO_2 versus Zr. A weak correlation between Cr and V suggests a similar source for both elements. The K/Al ratio correlates well with the ratio of illite/kaolinite.

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Weathering crusts, clay mineralogy and tectonic quiescence: preliminary results

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Deep weathering crusts of a kaolinitic nature have long been known in Russia and adjacent territories and their principal features were described and analysed in the western literature in an all but forgotten 60-year old paper by PETROV (1958). In brief, the kaolinitic weathering crust could show profiles that were complete, semi-complete or severely truncated, the latter suggesting a formerly much more extensive weathering cover. However, where an area has been subjected to intense tectonic forces, it was found that kaolinized rock could be found in sections tens and sometimes even hundreds of meters in thickness. Such occurrences occurred in elongated shapes, lacked distinctive chemical or mineralogical zonation and were described as “linear weathering crusts”, contrasting with the complete or semi-complete, distinctly zoned weathering profiles which were described as “areal weathering crusts”.

A kaolinitic weathering crust is prominently exposed in the banks of the River Tom, in Tomsk in west Siberia overlying near-vertical sandstones and siltstones of late Carboniferous age and overlain by horizontal siltstones and coals of Palaeocene age. These observations indicate that the age of the weathering is Mesozoic and are consistent with Petrov’s analysis that the kaolinitic weathering crusts in Russia and elsewhere formed during a period of unusual tectonic quiescence during the Lower Mesozoic. The remains of such kaolinitic weathering crusts are also found in numerous sites in western Europe and, bearing in mind that the proto-Atlantic only formed during the late Cretaceous, it might be anticipated that they occur in North America too.

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Smectite stability in alternating mudstone-sandstone facies from the Pennsylvanian Hoxbar Group (Anadarko Basin, Oklahoma)

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One of the most prolific sedimentary basins in North America is the Anadarko Basin located in the central part of the United States (Oklahoma and north Texas). It is also the deepest structural and sedimentary basin in the cratonic interior of the United States, containing approximately 12 km of Cambrian through Permian sediment in its deepest portion, with a total thickness of the Pennsylvanian strata reaching 3–4 km (RASCOE, 1962). These strata are chiefly consisted of marine and non-marine shale and sandstone, presenting one of the major hydrocarbon reservoirs in the Anadarko Basin. The studied Pennsylvanian shale and sandstone belong to the Hoxbar Group, which is a thick sedimentary unit made of multiple shaley horizons interbedded with sands and, occasionally, thin limestones (RASCOE, 1962).

The amount of detrital clays in sandstones is usually modest, owing to hydrodynamic sorting and other depositional processes, whilst in mudstones clay minerals are abundant and are mostly inherited directly from the original sediment (e.g. CLAUER et al., 1999). Illite-smectite (I-S) from the prograde diagenetic series is common in both lithologies and subtle changes in its crystal chemistry and component makeup may be considered as proxies of the continuously changing diagenetic conditions (e.g. ŚRODOŃ et al., 2000). If one assumes the uniform source of detrital clays, then the smectite evolution in such alternating series may result with (1) a similar specific composition of I-S in sandstones and adjacent mudstones, (2) lower smectite in I-S in sandstones compared to I-S of alternating mudstones, and (3) higher smectite in I-S in sandstones compared to I-S of alternating mudstones (e.g. HILLIER et al., 1996). The reasons for such dynamics are multiple and are generally related either to the differences in thermal stability of authigenic and detrital smectite or to enhanced flow rates in sandstones that promote illitization of smectite (e.g. MCKINLEY et al., 2003).

Two cores were sampled from a depth of about 3 km from which 66 shale and sandstone samples were studied using the X-ray diffraction as well as the automated and conventional scanning electron microscopy. The depositional environment of the Hoxbar Group along with diagenetic aspects of alternating shales and sandstones were investigated in detail. The latter presumably exercised a major influence on the evolution of smectitic clay assemblages and, given an increasing significance of Pennsylvanian strata of the Anadarko basin in the exploration of hydrocarbons a detailed knowledge of clay mineralogy of Hoxbar mudstones and associated sandstones becomes critical for predicting the distribution of high-quality reservoirs and for the exploration of their forming mechanisms. Our preliminary data shows that the average clay mineral content in sandstone is about 6 % compared to 35 % of clays in mudstone. In the latter, several generations of illite-smectite, including rectorite, dominate the clay fraction. On the other hand, clays in sandstone are illite-rich I-S with only minor rectorite component and kaolinite. This clearly shows a facies control on clay speciation but it also points to the effect of higher permeability of sandstone or, alternatively, the impact of the circulation of hot fluids facilitating higher diagenetic rates characteristic of an open diagenetic system. Such smectite dynamics in neighboring sandstone and mudstone layers may also suggest different rates of authigenesis of smectite in analyzed rock types, which is subject to further investigation.

Acknowledgments

This study was financed by the AAPG's Grants-In-Aid Program 2017 (Grants-in-Aid Fund) and 2018 (Eddie David Named Grant) as well as the TTU scholarship (Graduate Student Research Support for spring 2018).

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High-pressure methane adsorption on Cs-montmorillonite: experiments and Monte Carlo modelling

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Methane (CH_4) adsorbed or retained under high-pressure is abundant in various natural environments rich in clay minerals, such as sedimentary rocks and soils. Clay minerals are considered as one of the major contributors to a rock or sediment's mineral surface area and microporosity, where CH_4 can be adsorbed (TOPÓR, et al. 2017). There is no agreement, however, whether the interlayer of expandable clays is accessible for methane molecules or it is only the external surfaces and micro-porosity formed between individual grains or crystallites that provide adsorption sites.

The potential of CH_4 adsorption on clay minerals is usually investigated using a high-pressure adsorption measurement. This methodology, however, provides information only about excess amount of adsorbate on the surface with reference to the density of bulk gas that is not adsorbed. However, it is the entire amount of adsorbate present in the adsorbed gas volume (called absolute adsorption) that is the thermodynamically meaningful value and the ultimate aim of the measurement. In order to calculate the absolute adsorption from an excess adsorption isotherm, one should know the volume or density of adsorbed phase, which are not readily available from experiment.

In the present study, high-pressure CH_4 adsorption experiments were conducted on Cs-exchanged montmorillonite SAz-1 (Cheto, Arizona). The sample was dried in-situ at 210°C for 20 h to remove strongly-bound H_2O, then CH_4 adsorption was conducted at 25°C in a pressure range from 0 to 150 bar. A series of Gibbs Ensemble Monte Carlo simulations (MC) was performed using a simulation system consisted of two boxes. The first one was filled with two montmorillonite layers, Cs cations, and H_2O, which were described with CLAYFF force field (CYGAN et al., 2004); smectite d-spacing was fixed at various values, from 11.3 to 57 Å. The second simulation box was filled with pure CH_4 under controlled pressure; CH_4 was set as transferable between boxes to equilibrate the system. EH-TraPPE force field was used for CH_4 (CHEN & SIEPMANN, 1999).

Simulations' results showed that minimum d-spacing of 11.7 Å allows first methane molecules to enter the interlayer space. An increase in d-spacing, from 11.3 to 15 Å, resulted in not only greater adsorbed volume, but also higher density of intercalated methane. CH_4 density profiles in 11.3 to 12.5 Å-montmorillonite showed only one maximum, for 15 Å - two maxima, one on each side of the interlayer, and for 57 Å two maxima on each side, with the first one greatly prevailing. The volume of adsorbed phase remained relatively constant for different pressures, but varied with the smectite's d-spacing. Intermolecular van der Waals force, per one molecule in the interlayer are positive for 11.3, 11.7, and - partially – for 15 Å-smectite, negative for 12.1, 12.5 Å-smectite and for high-pressure region of 15 Å-smectite. The total Coulomb potential energy of the first box was found the lowest for 11.3 Å-smectite and then showed local minimum at 12.1 Å. These results indicate the energetic preference for the formation of intercalate with a certain number of CH_4 layers.

Excess adsorption isotherm obtained experimentally showed no hysteresis, with maximum excess adsorption on the level corresponding to the MC simulation with 12.1 Å-smectite. Density profiles obtained from MC were used to calculate the absolute adsorption from experimental isotherms. The calculated absolute adsorption varied greatly, depending on the density profile applied. Hence, it is of great importance to determine the type and dimension of interlayer or confined pore space that corresponds to the material actually analysed for high-pressure CH_4 adsorption.

Acknowledgments

This study was financed by National Science Centre, Poland (grant no. 2017/25/N/ST10/02034).

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Introduction to the Workshop NanoMin

Biogeochemical processes in modern sediments and soils are governed by the physico-chemical properties of mineral phases from which they are formed. Among them, sub-micron sized, particularly nanomineral solids, are common and widely distributed components in nature that comprise over 90 % of the reactive mineral surfaces. These particles, in the size range of 1 to 100 nanometers, of either abiotic or biotic origin, display unique structural, chemical and surface properties. Nanominerals and nanosized-mineral particles are important solids that govern the transport, deposition and the fate of the organic and inorganic compounds in nature, including the global carbon cycling and storage. Their reactivity is based on the processes of their formation, dissolution, and phase transformation, binding of organic and inorganic compounds, catalytic activity of their surfaces in modifying properties of chemical compounds, mutual interaction with other inorganic and organic particulates, and on their role in biomineralization processes at the nanoscale. The contribution that nanominerals and nanosized-minerals play in formation of sediments and soils and in geochemical processes in nature is still paltry investigated and should be better determined.

The purpose of this Workshop is to provide a comprehensive insight into the role of sub-micron, particularly nanosized mineral particles in the formation of recent sediments and soils/palaeosols and their significance in geochemical cycling of sedimentary organic materials and trace metals in sediments/soils/palaeosols of the Adriatic region. In addition, authigenic formation and morphogenesis of submicron sized and nanostructured mineral phases with their role in biogeochemical processes will be also addressed. The workshop will present the most significant research results that have been obtained within the project of the Croatian Science Foundation under the title *Nanominerals in sediments and soils: formation, properties and their role in biogeochemical processes* (NanoMin, 2504).

The workshop is organized by the Croatian Clay Mineral Society and it is sequel to the 9th Mid-European Clay Conference (MECC 2018), Zagreb, Croatia, September 17-21, 2018.

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Understanding the (paleo)soils: From palaeoenvironmental reconstruction to the role of iron oxides and soil organic matter on the formation of the surface physicochemical properties and the aggregation processes

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A multi-proxy analytical approach (MPAA) in the investigation of (palaeo)soils that involves a detailed analysis of soil micromorphology, soil physics and chemistry, geochemistry, and bulk and clay mineralogy is crucial for the determination of the palaeoenvironment in which they were formed. The determination of the soil mineral composition and their surface properties that control the formation of soils by aggregation processes is necessary to understand their response to environmental changes (BRONICK & LAL, 2005). Soil aggregation is a complex process, which involves rearrangement of submicron- and micron-sized mineral particles into larger clusters by mutual physico-chemical and biological interactions between the mineral surfaces, various organic and inorganic compounds and microorganisms (SIX et al., 2004). Humic compounds are omnipresent in soils and they designate the most important compounds covering the surfaces of the minerals, particularly iron oxides and clay mineral particles (BALDOCK & BROOS, 2012). This lecture aims to demonstrate the significance of MPAA in three different cases, from profile description and palaeoenvironmental reconstruction, to the role of iron oxides and soil organic matter on the formation of the surface physicochemical properties and the aggregation processes. It is based on our previous (DURN et al., 2015; DURN et al., 2017) and current research within the NanoMin project (grant 2504, Croatian Science Foundation).

Case 1: A polygenetic soil formed on Late Glacial Loess on the Island of Susak

The complete polygenetic profile (A-2C1-2C2-3Btb-4Ck) was formed through both normal pedogenesis and erosion/sedimentation-driven pedogenesis, and is a result of the interaction of the sediments (loess) with environmental conditions from the Late Glacial throughout the Holocene (Fig. 1). This profile bears valuable imprints of climate, vegetation, land surface, and land use changes in this part of the Adriatic area for the time period covering the past 16 ka. A high-resolution approach enabled schematic reconstruction of polygenetic formation of the soil profile while the results of clay fraction analysis and micromorphology in particular helped to understand the genesis of the investigated soil at the Susak Island (*e.g.* inherited vs. pedogenic clay).

Case 2: (Paleo)soils formed in contrasting pedoenvironments (oxidizing vs. reducing) on pure Cretaceous limestones in Istria

Terra Rossa soils formed in an oxidizing pedoenvironment, while Cretaceous greenish-grey palaeosols (GGP) formed in a reducingone. While kaolinites and illitic material are dominant clay mineral phases in the clay fraction of Terra Rossa, the main clay mineral phases in GGP are illitic material and ordered and irregularly oriented illite/smectite mixed layer minerals. Terra Rossa soils are slightly enriched in Co and Pb and significantly enriched in REE compared to GGP. The important difference in the total REE content in analysed Terra Rossa soils can be attributed to the REE content of both parent carbonate rocks (their insoluble residues) and different external materials which have contributed in the genesis of Terra Rossa (loess, flysch, bauxite), modified by weathering processes which favour LREE enrichment. Sequential extraction analysis showed that Mn, Co and Pb, mainly bound to the reducible fraction, are potentially the most mobile trace elements in Terra Rossa. , The enrichment of GGP in Cd, Sb, Ni, V and especially in U and Mo is considered typical of reducing environments (Fig. 2). Variation of the total REE content in GGP is much narrower compared to Terra Rossa soils. Total REE content in GGP is dominated by the residual fraction and probably also reflects parent materials (insoluble residue of limestone, aeolian and volcanic dust), modified in an acidic and reductive marshy pedoenvironment which favours HREE enrichment. Cd, Ni and Co, mainly bound to the adsorbed fraction are potentially the most mobile trace elements in GGP.

Case 3: The role of iron oxides and soil organic matter (SOM) on the formation of the surface physicochemical properties and the aggregation processes of the Terra Rossa and the Calcocambisol from Istria

Terra Rossa is the most common type of soil in Istria, an archetypal example of a non-isolated karst terrain that has been affected by karst processes, (neo)tectonic activity and contributions of external materials since the Late Tertiary. Their clay size fraction contains hematite as a dominant, and goethite as a minor iron oxide. The second most important and insufficiently investigated soil type in Istria is the Calcocambisol, a brown soil on limestone and dolomite. In comparison with Terra Rossa, this soil type contains a higher amount of organic matter while goethite was determined as the only well-crystallized iron oxide. The aim was to determine the character and the role of SOM and iron oxides on the formation of the surface physicochemical properties, electrophoretic mobility (EPM), specific surface area (SSA), and cation exchange capacity (CEC) of mineral particles that are main constituents of submicron- and micron-sized aggregates in selected Terra Rossa and Calcocambisol samples from B horizons. Specifically, the ultimate goal is to identify these properties on original soils and on the samples from which the SOM and the iron compounds were selectively removed. This study endeavours to contribute new evidence on the role of SOM and iron oxides in the formation of surface properties of mineral particles and to determine their role in the process of aggregation in these type of soils (Fig. 3).

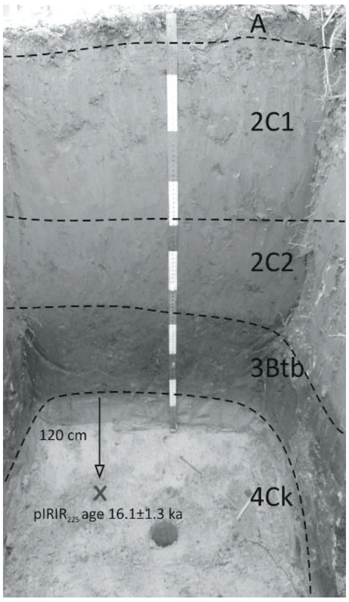

Figure 1. Polygenetic soil profile at the Susak Island (From: DURN et al., 2017).

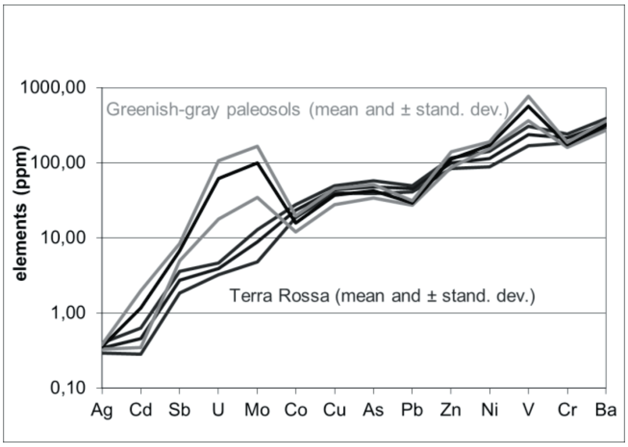

Figure 2. Distribution of trace elements in Terra Rossa and greenish-gray paleosols.

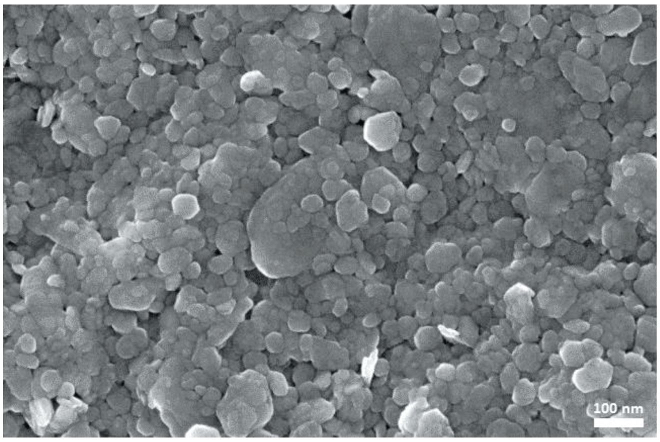

Figure 3. FESEM photomicrograph of Terra Rossa (submicron-sized fraction) after removal of iron oxides. A significant part of submicron-sized fraction appear in nanosized range.

Acknowledgments
This work has been fully supported by Croatian Science Foundation under the project 2504 (NanoMin).

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Size-related mineralogical and surface physico-chemical properties of inorganic colloidal particles in recent marine sediments of the Adriatic

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Mineral particles play a major role in biogeochemical processes in nature, particularly in binding, transport and deposition of different organic and inorganic compounds. Among them, the colloidal mineral phases, particles in the submicron- and the nanosized range represent the most reactive mineral surfaces in the environment (HOCHELLA et al., 2008; TANG et al., 2009; PLATHE et al., 2013). Through complex physico-chemical processes associated with their surfaces, these solids affect bioavailability, toxicity and the fate of the associated inorganic and organic compounds. Their unique surface reactivity is a consequence of their size-related structural and surface physico-chemical properties.

In marine sediments, the colloidal mineral fraction mostly consists of clay minerals, metal oxides and oxyhydroxides, sulphides, and, sporadically, carbonates (PERRET et al., 1994). Carbonate minerals are rarely found in the nanosized range and mostly occur as lithogenic and biogenic fragments in coarser fractions (BUFFLE et al., 1998). The results obtained in this study show the mineral composition, occurrence, distribution and the surface physico-chemical properties; specific surface area (SSA) and cation exchange capacity (CEC) of different size fractions collected in various sedimentological environments in the Adriatic Sea. The influence of organic and inorganic surface coatings on the reactivity of mineral surfaces was investigated. A detailed mineralogical investigation revealed significant changes in the composition of mineral particles in the clay fraction. The obtained results revealed presence of nanosized particles mainly in the form of microaggregates in strong associations with organic matter, difficult to disrupt even despite of chemical treatments. The authigenic precipitation seems to be the main mechanism leading to a more significant share of carbonates in the colloidal size range. In sediments where weathering of carbonates is the main source of their origin, their occurrence was limited to coarser size fractions and clay minerals were the dominant mineral phase in the colloidal size range. These changes in the mineralogical composition were reflected in the surface physico-chemical parameters. As a result, size fractions with predominance of submicron-sized clay minerals showed a significant increase in SSA and CEC with particle size lowering.

9th Mid-European Clay Conference – MECC 2018

Acknowledgment
This work has been fully supported by Croatian Science Foundation under the project 2504 (NanoMin).

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Formation of the authigenic cements in aquatic sediments through precipitation processes at the nanoscale - isotopic and FESEM study

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The traditional view on carbon cycle assumes that CO_2 is removed from the atmosphere by two major sinks, i.e. oceans and the biosphere. Terrestrial carbon sink in cements precipitated from groundwater, from interstitial water in recent sediments or from surface water (tufa) has been largely underestimated or neglected. Recent studies showed, however, that the magnitude of authigenic carbonate precipitation might be immense, so that it can be considered as the third major global C sink. Knowing this, the importance of identification and quantification of secondary carbonate becomes apparent on local, regional and global scale. While quantification of carbonate cements is rather simple in siliciclastic sediments, it remains challenging in carbonaceous environments.

Isotopic tools were proven to be efficient for differentiation between primary (marine) carbonate and authigenic cements produced in organic-rich sediments or from terrestrial groundwater. The C isotopic composition of marine carbonate (limestone, dolostone) differs significantly from that precipitated from high-alkalinity interstitial solutions where the dissolved inorganic carbon derives at least in part from the decomposition of organic matter. Namely, organic tissues are depleted in ^{13}C compared to marine and atmospheric CO_2 because of preferential uptake of isotopically light C from the environment and complex isotope fractionation accompanying biological processes.

Our study deals with precipitation of authigenic carbonate in recent aquatic carbonaceous sediments formed on karstic terrains in a range of environments – from freshwater (lacustrine tufa, Krka river), transitional (Neretva river delta), to marine lakes and coastal marine sediments (islands of Mljet and Dugi otok, Croatia). We analysed isotopic, geochemical and morphological characteristics of sedimentary carbonate and organic matter, and using isotopic tools, assessed the transfer of carbon between dissolved and solid pool. The CO_2 cycling in lakes and reservoirs, as well as organic rich marine sediments was largely dominated by biological and biogeochemical processes. Diagenetic degradation of sedimentary organic matter represents a complex suite of microbially-mediated and abiotic processes, that mineralise organic carbon to the CO_2 or CH_4, which undergo further processing by microbial communities and provide a source of dissolved inorganic carbon for precipitation of carbonate cements. However, in organic-rich sediments with multiple C sources (soil, lithic carbonate, land vegetation, aquatic biota) and changing redox conditions, the isotopic signatures of dissolved carbonate vary not only because of different C sources, but also because of complex diagenetic processes that remove or add dissolved inorganic carbon (DIC) from/to the interstitial solution, and fractionate DIC isotopes either in same or in different directions (i.e. toward more positive or more negative δ values). At the same time, the C isotope fractionation during precipitation of calcite remains rather stable irrespective of the temperature and precipitation rate and authigenic carbonate reflects the isotopic composition of DIC ($\delta^{13}C$) within approximately ±1 ‰. Therefore, the C isotopic composition of authigenic carbonate in organic-rich sediments is not unique or exclusive for a certain environment, but depends on the combination of processes that simultaneously or consecutively affect the concentration and $\delta^{13}C$ of DIC. Therefore, additional identifiers of authigenic carbonate in freshwater sediments from carbonaceous settings are necessary for its unequivocal identification and quantification.

Acknowledgments

This study was funded by the Croatian Science Foundation (project 2504 NanoMin - Nanominerals in sediments and soils: formation, properties and their role in biogeochemical processes), Slovenian Research Agency (programme P1-0143) and European Commission (Horizon 2020, project MASSTWIN - Spreading Excellence and widening participation in support of mass spectrometry and related techniques in health, the environment, and food analysis, grant agreement No. 692241).

Nanosized and nanostructured mineral phases from recent sediments and soils of the Adriatic region

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This presentation aims to demonstrate the appearance of nanosized and nanostructured mineral phases determined in different modern marine and lacustrine sediments of the Adriatic region (Fig. 1) and in soils situated on carbonate rocks along the Adriatic coast. Special attention was paid to determining the type of nanominerals and nanosized mineral phases and their unique structural and morphological features at the nanoscale. The results obtained show that their appearance in sediments and soils can be used to determine the physico-chemical conditions that prevailed in the environment during their formation. In addition, the occurrence of newly formed nanomineral particles allow us to determine the early diagenetically driven changes that govern formation and phase transformation of nanosized mineral particles in environment. The role of nanomineral phases in the cycling of trace elements in investigated sediments will be also addressed. Biologically induced formation of submicron-sized, nanostructured and hierarchically organized biomineral structures built up of anhydrous carbonates, particularly aragonite and calcite will be presented. Finally, the role of reaffirmed non-classical crystal-growth mechanisms, especially the particle-mediated, nanoscale aggregation route where nanostructured mineral phases are formed through the aggregation of preformed nanosized particles will be discussed.

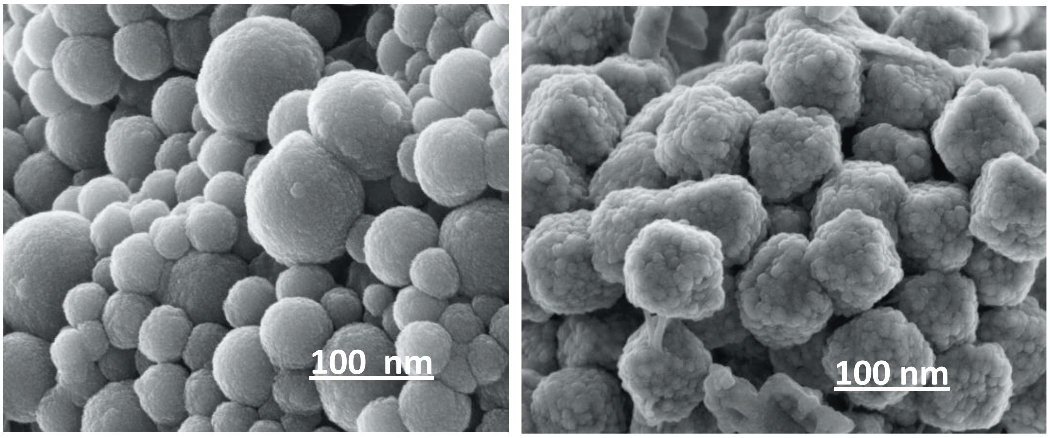

Figure 1. FESEM photomicrographs showing morphological features of the authigenically precipitated nanosized vaterite prevailing in the Kuti Lake sediments, the Neretva River Delta (left) and nanosized framboidal pyrite clusters from the Malo jezero, Mljet island (right).

Acknowledgments
This work has been fully supported by Croatian Science Foundation under the project 2504 (NanoMin).

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FIELD TRIP
GUIDE BOOK

FIELD TRIP TO HRVATSKO ZAGORJE

Zagorje is located in the northwestern part of the Republic of Croatia and occupies a total area of about 1,900 km^2. It is a hilly terrain surrounded by the Medvednica and Kalnik Mts. to the south, the Varaždin-Toplica, the Ravna Gora and the Maceljska Gora Mts. to the north, and the Sutla and Drava Rivers to the west and east, respectively. It has rich natural, cultural and historical heritage. Field trip includes 5 geological stops combined with historical and geological heritage (Fig. 1):

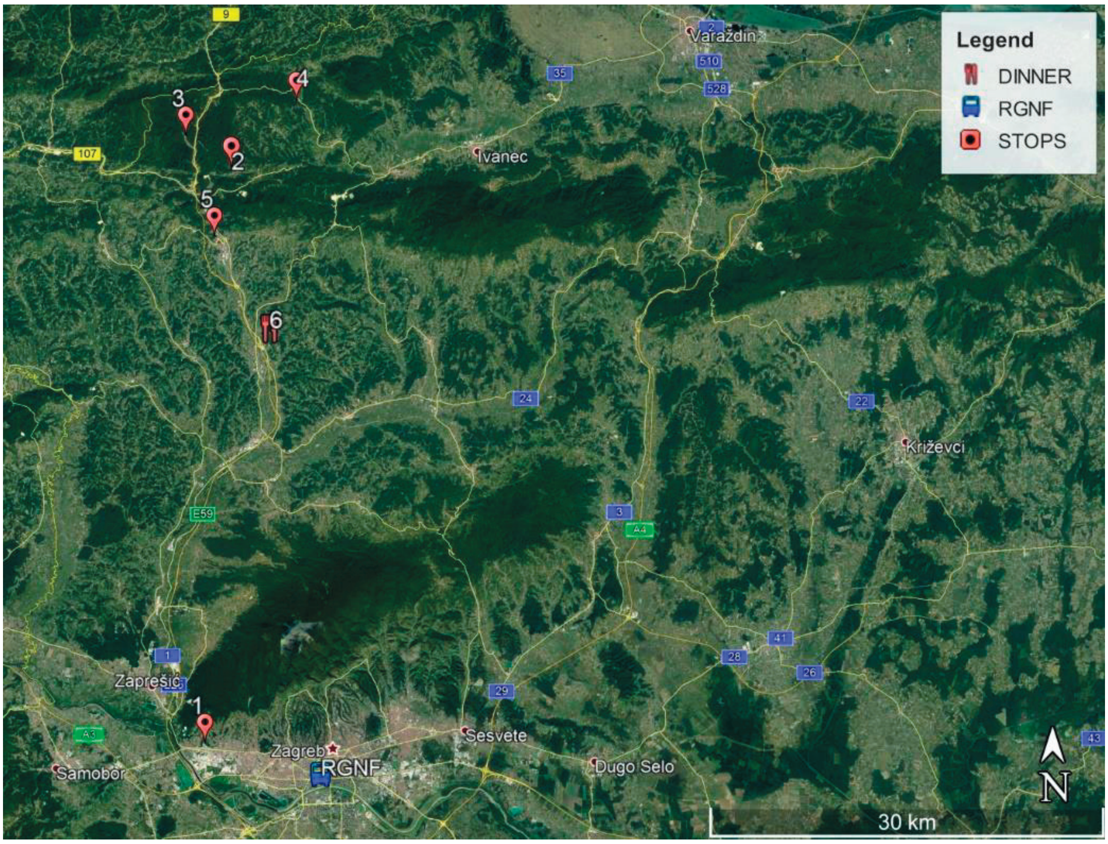

Figure 1. Geographical map of Hrvatsko Zagorje with field trip stops (source: http://www.google.com/earth/download/ge/).

1. Landslide Kostanjek. Landslide Kostanjek is the largest (1 km^2) active landslide in Croatia, located in the urbanized area (ca. 300 houses) in the westernmost part of the Croatian capital Zagreb. Landslide was initiated in 1963 by exploitation of Panonnian and Sarmatian marl for cement industry situated at the foot of the slope. It is reactivated, translational, and extremely slow to very slow landslide, with depth of ca. 60 meters. Sliding mass is ca. 32 million cubic meters. The landslide is equipped with a sophisticated monitoring system providing a better understanding of the sliding.

2. Zeolitized pyroclastics of the Donje Jesenje. In the northwestern part of the Hrvatsko Zagorje, at several locations on Maceljska Gora Mt., Lower Miocene volcanoclastic deposits occur. The best outcrop of volcanoclastics is in the Donje Jesenje quarry. These sediments are a result of the submarine volcanic activity between the Egenburgian shelf and shoreface. Volcanoclastic deposits have a variable primary composition, and contain various volcanic glass alteration products, including zeolites, clay minerals and SiO_2 phases. Clinoptilolite is the most abundant zeolite in these deposits. Mordenite and analcime are also present. Clay minerals are represented by smectites and celadonite.

3. Glauconitic sandstones of the Vučji Jarek. The deposits of Macelj sandstones were formed on the shoreface under the influence of tides. Macelj sandstones, some of them containing glauconitic materials, belong to the Vučji Jarek Mb. as the lowermost part of the Macelj Fm. The Macelj Fm. deposits were formed in the Eggenburgian and Early Ottnangian.

4. Trakošćan Castle and bedded conglomerates and sandstones of Trakošćan. One of the most attractive castles in Croatia dates back to the 13th century (although the first written mention of the toponym "Trakošćan" is dated to 1334). Together with surrounding buildings and forest park with a lake it is protected as a historical entity. Bedded conglomerates and sandstones from the Early Miocen are located at the base of the southwest margin of the Trakošćan Castle.

5. Kraneamus, Krapina Neanderthal Museum and Site Hušnjakovo is located near the world famous site of the Krapina Neanderthals "Hušnjakovo". The exhibition is set up as a time machine through the history of the Universe, the Earth and Man, leading up to the present day, and lays special emphasis on the Neanderthal period.

The Neogene of Hrvatsko Zagorje

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The origin of the oldest Neogene rocks of the Hrvatsko Zagorje region is related to the coastal area of the Central Paratethys in the Late Eocene when, due to the continental collision of Eurasia with Africa and India, the Tethys split into Paratethys and the Mediterranean Sea (RÖGL, 1996, 1998). In the Late Eocene, Oligocene and Early Miocene, the marine sedimentation continued only in the northern part of Hrvatsko Zagorje, that is, in the Hrvatsko Zagorje Basin (HZB - north of the Kalnik Mt.). During this period, the southern part of Hrvatsko Zagorje, as a northwestern part of the North Croatian Basin (NCB) was predominantly the land area while the marine sedimentation started in the Early, and, according to some geologists, only in the Middle Badenian when these two basins had been connected (AVANIĆ et al., 1990; ŠIMUNIĆ, AN. et al., 2000; PAVELIĆ et al., 2001, 2002; VRSALJKO et al., 2006; ĆORIĆ et al., 2009; AVANIĆ, 2012; BRLEK et al., 2016; MARKOVIĆ, F., 2017; PAVELIĆ & KOVAČIĆ, 2018).

The oldest sedimentary rocks on the surface are located in the northern part of Hrvatsko Zagorje in the area of the Ravna Gora Mt. These Oligocene–Miocene rocks overlie the shallow water marine sediments of the Keglević Fm. of the Middle to Late Eocene age (ŠIMUNIĆ, AN. et al., 2000). After the Eocene there occurred a short emersion followed by marine transgression during the Kiscellian stage characterized by deposition of sediments of the Meljan Fm. In the beginning, the clayey limestones and calcarenites reflect deposition in the littoral and afterwards, until the Early Egerian, deposition continued in the prodelta environment with marls and sandstone intercalations (AVANIĆ et al., 2007). A sedimentation with prograding tendencies continued into the Late Egerian with prodelta and coastal deposition of sands and marls, followed by the delta pyroclastics and conglomerates of the Golubovec Fm. The significant supply of terrigenous material is also indicated by the fragments of coal that have been eroded from the floodplains or delta plains and transported into the coastal environment. The existence of several layers of brown coal is recorded in numerous coal mines in the area between Pregrada and Krapina as well as along the Strahinščica and Ivanščica Mts., and the eastern parts of the Kalnik Mt. (AVANIĆ et al., 1990; MARKOVIĆ, S., 2002). Due to the collision of the Adriatic plate and the European foreland (SCHMID et al., 1989), the regional stress characterized by the main NS compression axis with EW extension occurred during the Oligocene and Miocene. Within the stress zone of the Hrvatsko Zagorje Basin, the Donat and Rogaška fault systems with dextral strike slips were formed, representing the eastern continuation of the Periadriatic lineament (ŠIMUNIĆ, AN. & PAMIĆ, 1993; TOMLJENOVIĆ & CSONTOS, 2001). Associated to these fault systems is occurrence of synsedimentary volcanism in the Egerian (andesite and pyroclastic rocks of the Golubovec Fm.) and Eggenburgian (tuffs of the Macelj Fm.).

After the emersion at the end of the Egerian in the HZB, the onset of the Eggenburgian was marked by a transgression and deposition of sands, glauconitic sands and pyroclastics of the Vučji Jarek Mb. of the Macelj Fm. in the coastal environment, coinciding with the sea level rise in the Central Paratethys (STEININGER & WESSELY, 2000; AVANIĆ, 2012). Further relative sea level rise in this area caused the deposition of clayey and sandy silts of the transitional zone between the shelf and the shoreface environment of the Čemernica Mb. In the Late Eggenburgian, the uplifted parts of Strahinščica, Ivanščica and Ravna Gora Mts. were intensely weathered. The rivers had eroded and transported the coarse-grained terrigenous material that was finally deposited in the fan delta, prodelta, and shoreface environments (Lipni Vrh Mb.). At the end of the Eggenburgian and beginning of the Ottnangian there was a further rise of the sea level between the shelf and the coastal area under the tidal influences and the presence of volcanic activity (Vrbno Mb.). Sands deposited in the coastal area were characterized by cross-bedding while those accumulated on tidal flats and in tidal channels contain intercalations of layers and laminae of silts and clay. The transitional zone is characterized by marls intercalated with sandstone while only marls accumulated on the shelf. Volcanic activity at the end of Eggenburgian is indicated by tuffs, and bentonite clays originated from the subsequent alteration of the pyroclastics of the Vrbno Mb. During, and, especially, in the Late Ottnangian, deposition of calcitic silts and tuffs was followed by silty sands of the transition zone of the Bednja Fm., indicating a regressive sequence. The further relative sea level fall has been recorded in the Karpatian by the deposition of sand and gravel in the coastal area (Crkovec Fm.).

During the Ottnangian in the area of Kalnik and Medvednica Mts. (NCB), gravels with lens of sand and silts of the alluvial environment of Daranovci Fm. have been deposited (AVANIĆ et al., 1995; PAVELIĆ et al., 2001). The prevalence of coarse-grained sediments in the Early Ottnangian is related to the occurrence of the main normal faults, i.e. the extensions within the basins, accompanied with formation of half-graben of the early syn-rift phase (PAVELIĆ et al., 2001). From the Late Ottnangian to the Karpatian (ĆORIĆ et al., 2009) and, according to the latest data, to the Middle Badenian (MARKOVIĆ, F., 2017; PAVELIĆ & KOVAČIĆ, 2018) a freshwater lake developed in that area (Glavnica Fm.). In the lower part of the Glavnica Fm. congerian limestones with coal layers (Vukov Dol Mb.) represent the deposition on the littoral, while marls and tuffs were deposited in the deeper lake, as well as marls with laminae and layer sands in prodelta (Koščević Mb.). Mostly the upper part of the formation, delta front and prodelta conglomerates with lenses and intercalations of sands and siltites of the Franci Mb. occur (AVANIĆ, 1997). The occurrence of pyroclastic rocks in the Ottnangian, Karpatian and Early Badenian was related to syn-rift processes (PAVELIĆ et al., 2001; MARKOVIĆ, F., 2017). The depositional sequence in the NCB from the littoral, through the deeper lake to the delta sediments suggests the the sucession of deepening and subsequent shallowing. Due to the Early Badenian transgression in the Central Paratethys (RÖGL, 1996; SANT et al., 2017) in the area of the HZB, after a short emersion, there was a period of deposition of coarse-grained material in the shoreface area and formation of the Trstenik Mb. (AVANIĆ, 2012). It was later followed by a further deepening characterized by a deposition of marls in the shelf area of the Vejalnica Fm. By this transgression both the HZB and the NCB have been connected. The transition from the lacustrine into the marine deposition was gradual (AVANIĆ, 1997). Depending on the local tectonics and sea level oscillation in the area of the Hrvatsko Zagorje region during the Middle and Late Badenian the coastal parts were characterized by biocalcirudites and biocalcarenites of the Vrapče Fm. while in the offshore area marls of the Vejalnica Fm. prevailed. More rarely, marls may contain intercalations of coarse-grained sediments that represent shallow water material reworked by storms and transported by strong currents toward the offshore (AVANIĆ, 1997).

At the end of the Badenian, isolation of the Pannonian Basin started which in the beginning of the Sarmatian resulted by formation of a marine environment characterized by reduced salinity. Sarmatian sediments in the Hrvatsko Zagorje region usually conformably overlie Badenan sediments. They are represented by shallow-water conglomerates, calcarenites and limestones of the Pećinka Fm. or by horizontally laminated pelitic sediments of the Dolje Fm. deposited in somewhat deeper marine environment. The very end of the Sarmatian is characterized by shallowing of the marine environment due to the basin inversion (TOMLJENOVIĆ & CSONTOS, 2001). Pannonian sediments mostly conformably overlie Sarmatian deposits, and indicate a new transgressive-regressive cycle (PAVELIĆ & KOVAČIĆ, 2018). Their deposition took place in the newly formed brackish Lake Pannon. The oldest Pannonian sediments in the southern part of Hrvatsko Zagorje are composed of the platy clayey limestones of the Croatica Fm. deposited in the lake littoral. These sediments overlie sands with pebbles of the St. Matej Mb. deposited in the delta environment only in the north part of the Medvednica Mt. Clayey limestones of the Croatica Fm. gradually change into marls of the Medvedski Breg Fm. deposited in a deeper lake environment. At the beginning of the Pannonian the river clastic systems prograded from the northern and northwestern directions in the northern part of Hrvatsko Zagorje, spreading in the Middle Panonnian to its southern part forming sandy to silty sediments of the Andraševec Fm. Their accumulation commenced in a deeper lake environment, indicating the onset of the closing of the lake. The late Pannon Lake depositional phase was characterized by a regression indicated by predominantly sandy sediments of the delta of the Nova Gradiška Fm. That ended in the latest Pannonian by sedimentation of the delta and alluvial plain sediments of the Pluska Fm. During the Pliocene the area of Hrvatsko Zagorje was an alluvial plain with minor freshwater lakes and swamps. Geological map of the area is shown on Fig. 2, while geological column is on Fig. 3.

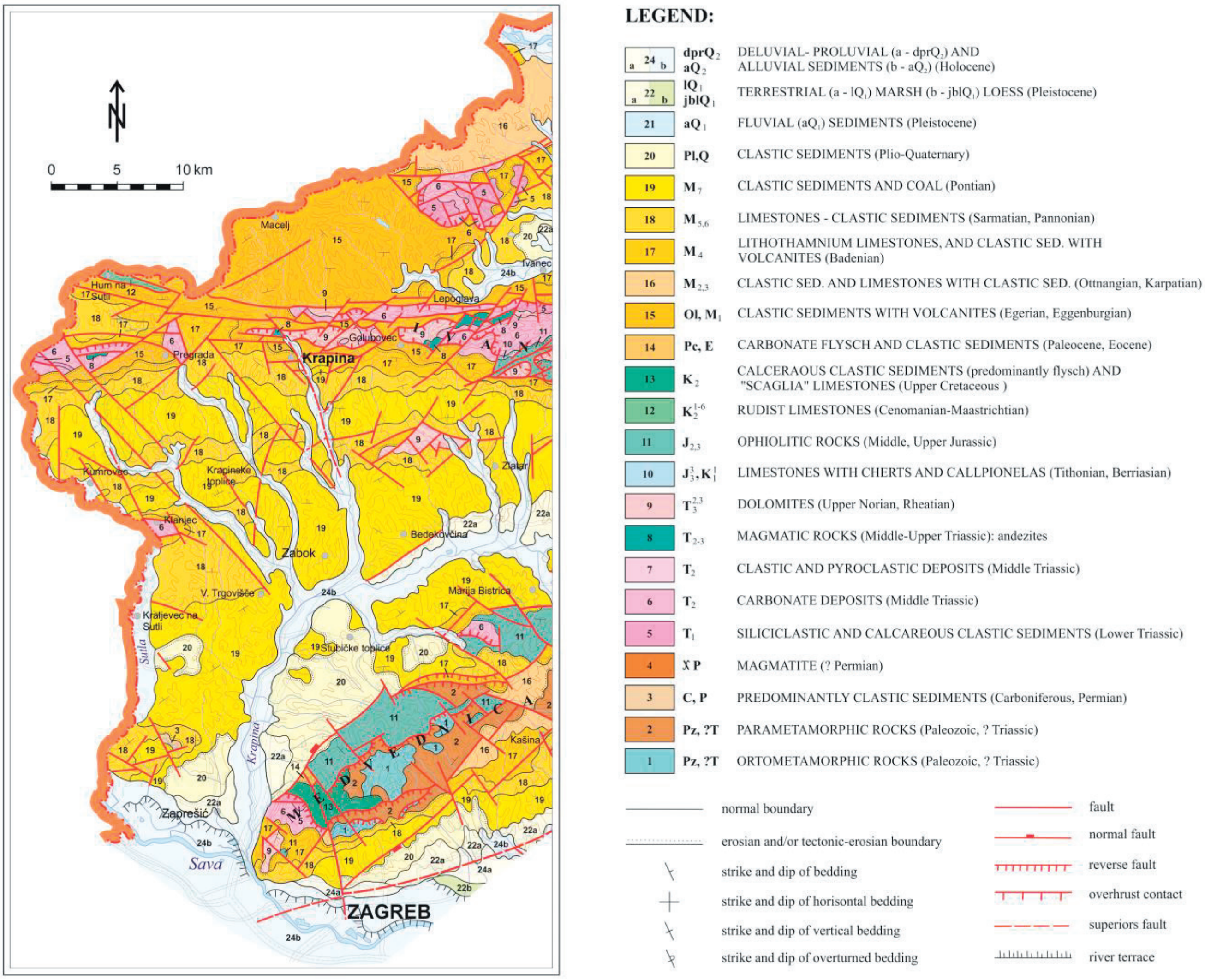

Figure 2. Geological map of the northwestern part of Croatia modifed according to the Geological Map of the Republic of Croatia 1:300000 (HGI-CGS, 2009).

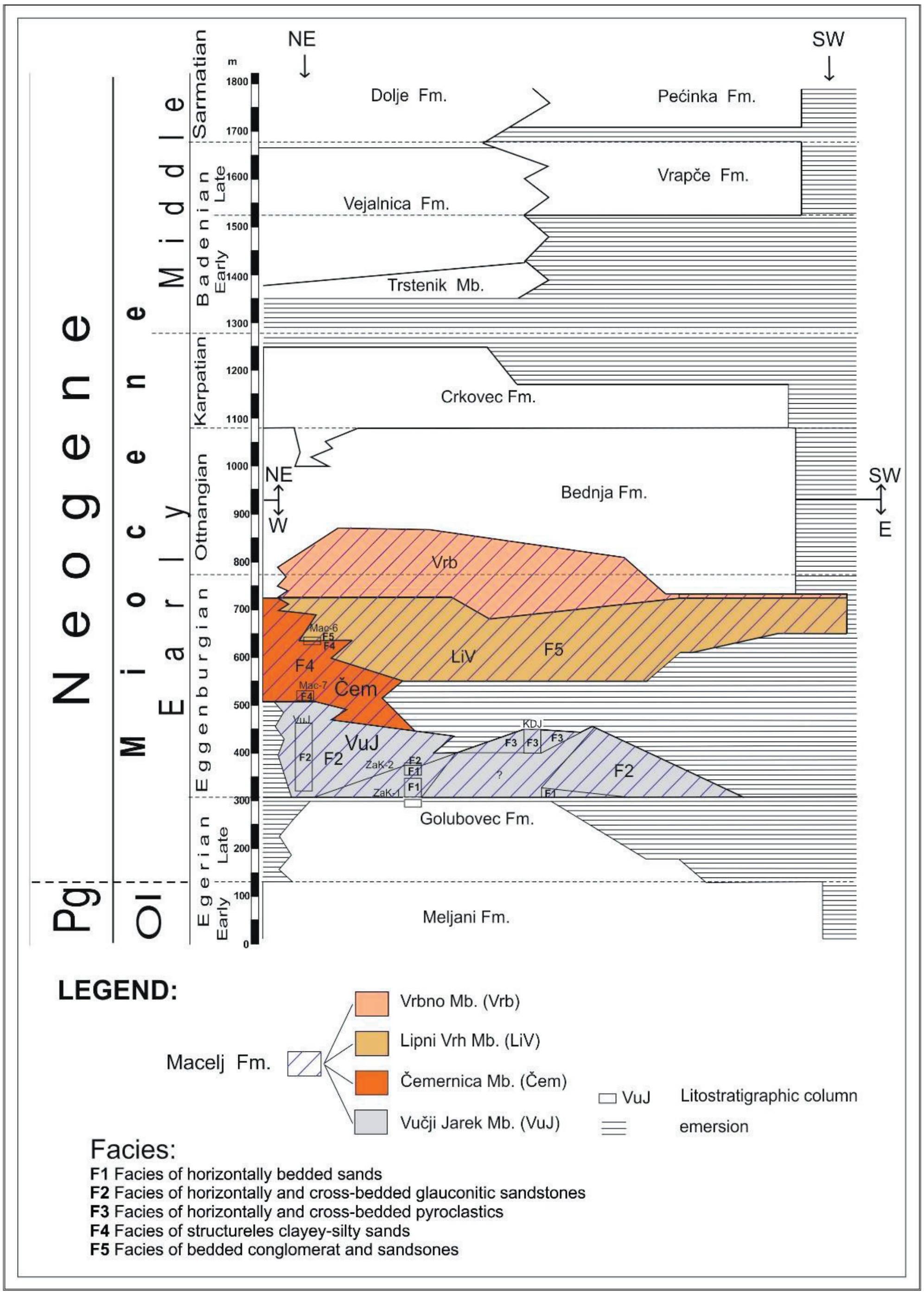

Figure 3. Schematic column of the Oligocene - Middle Miocene lithostratigraphic units of Hrvatsko Zagorje Basin (modified after AVANIĆ, 2012).

STOP 1: Landslide Kostanjek

Martin Krkač[1], Snježana Mihalić Arbanas[1], Ines Štimac[1], Jasmina Martinčević Lazar[2], Karin Wriessnig[3] and Marta Mileusnić[1]

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The Kostanjek landslide is the largest landslide in the Republic of Croatia. It is a reactivated deep-seated translational landslide located in the urbanized area of the City of Zagreb at the base of the southwestern slopes of Medvednica Mt. (Fig. 4). The sliding surface is developed in Sarmatian laminated marl, characterized by alternation of very thin light and dark laminae known as varves (according to WEINHEIMER & BIONDI, 2003). Displaced mass above the Sarmatian sediments consist of Lower Pannonian clayey marls with thin limestone layers and Upper Pannonian massive clayey marls. The width of the displaced mass is 960 m, and the total length of the Kostanjek landslide is 1.26 km. The maximal depth of the sliding surface is 90 m, according to interpretation of ORTOLAN & PLEŠKO (1992). The total landslide area is approximately 1 km^2, and the volume of the sliding mass is evaluated to be 32×10^6 m^3 (STANIĆ & NONVEILLER, 1996). Since its activation in 1963, Kostanjek landslide has caused substantial damage to buildings and infrastructure in the residential (Fig. 5) and in industrial zones. The deep-seated landslide was caused by anthropogenic factors, mainly by excavations in a marl quarry placed in the toe part of the landslide (Fig. 6). Uncontrolled blasting during the 1960s and 1970s in the marl quarry and the limestone quarry, placed approximately 1 km to the north from the upper part of the landslide, were also important destabilizing factors. Surface deformations are mostly expressed as ductile deformations with rare opening of cracks, even at the landslide boundaries. Despite extremely slow to slow landslide movements for 52 years, the risk in the area of the Kostanjek landslide is very high for residential properties (approximately 300 single-family houses and infrastructure networks are placed on the moving landslide mass).

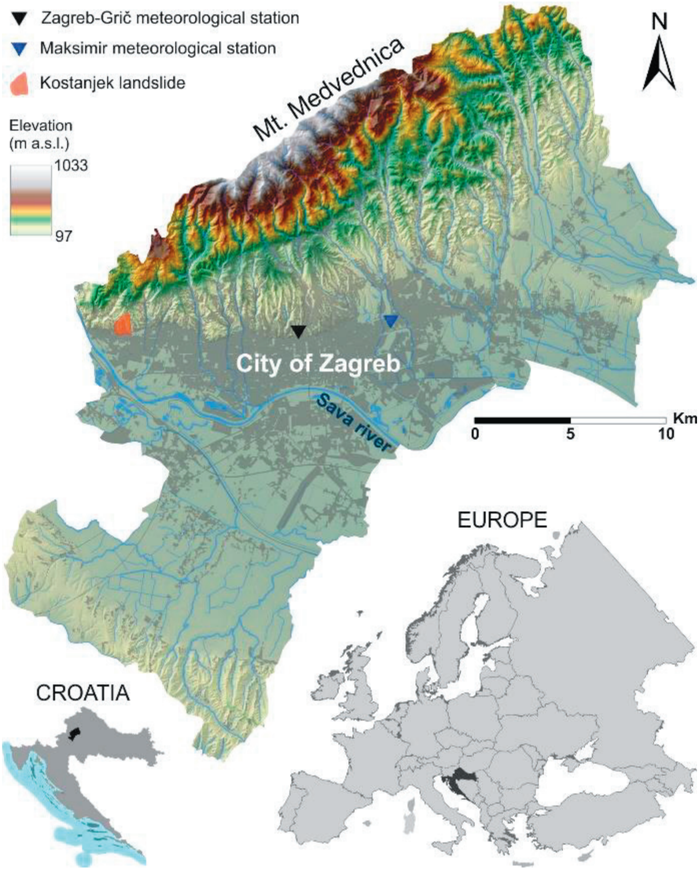

Figure 4. Location of the Kostanjek landslide and the meteorological station Zagreb-Grič (KRKAČ et al., 2017).

Figure 5. Damage caused by sliding (photo by D. Tibljaš).

Monitoring system

The Kostanjek landslide monitoring system was established in the framework of the scientific Japanese-Croatian bilateral SATREPS FY2008 project „Risk Identification and Land-Use Planning for Disaster Mitigation of Landslides and Floods in Croatia“, with the main objective of landslide mitigation though the development of an early-warning system (MIHALIĆ ARBANAS et al., 2013). In the period 2011–2014, multiple sensor networks (Fig. 6) were set up for continuous observations of (1) displacement (Global Navigation Satellite System or GNSS stations, extensometers, borehole extensometers), (2) hydrological properties (pore pressure gauges and water level sensors in boreholes and domestic wells, water level sensors at outflow weirs), and (3) external triggers (rain gauge and accelerometers). The majority of monitoring equipment is installed at a central monitoring station, located in the central part of the Kostanjek landslide (Fig. 6).

Analysis of monitoring data from all GNSS stations at showed similar patterns of movements across the entire landslide area, with the maximal velocities in the central part of the landslide and the lowest velocities along the landslide boundaries (KRKAČ, 2015). The total surface displacement in the period 2013-2016, measured by GNSS in central part of lanidslide was 440 mm. The displacement mainly occured durring the six periods of faster movements. The maximal observed velocity during the periods of faster movement was 3.3 mm/day, while during the periods of slower movement, the landslide velocities were up to 3 mm/month (0.1 mm/day). All periods of faster movement occurred as a consequence of groundwater level (GWL) rising (Fig. 7). The minimal observed GWL depth at the central part of the lanidslide was 10.5 m, and the maximal GWL depth was 19.03 m. Altogether, 17 periods of GWL rise occurred, during which GWL relatively changed up to 5.25 m. 12 of the 17 periods of high GWLs correspond to six periods of faster displacement. All GWL rising periods occurred after periods of intensive precipitations and snowmelt (Fig. 7).

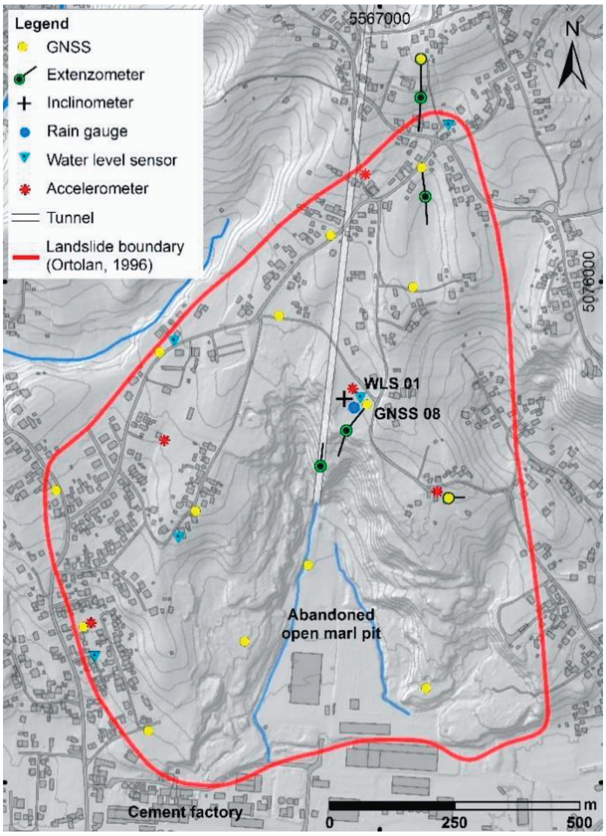

Figure 6. Multiple sensor networks at the Kostanjek landslide (KRKAČ et al., 2017).

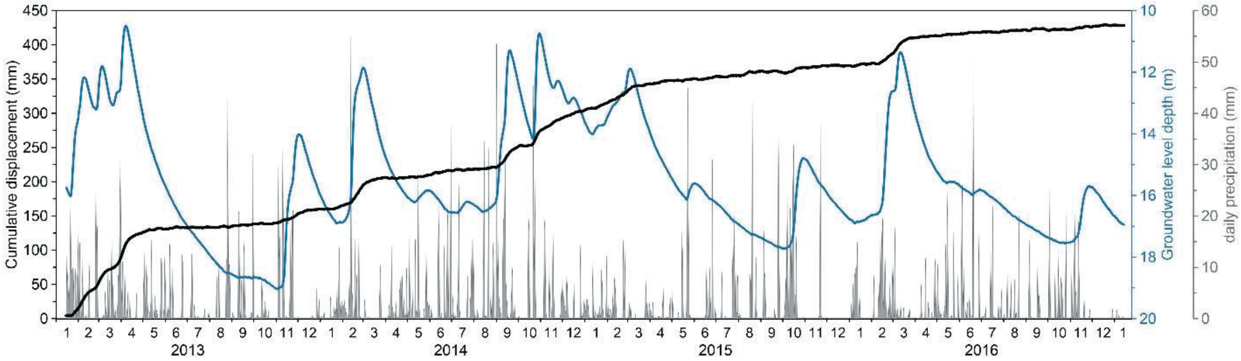

Figure 7. Displacements and groundwater level depths measured at the central monitoring station of the Kostanjek landslide and 1-day antecedent precipitations measured at Zagreb-Grič meteorological station.

Clay mineralogy

The slip surface in the mid-part of the Kostanjek landslide has been identified by KRKAČ (2015) using inclinometer measurement in the B-1 borehole to be in the Sarmatian unit, at the depth of 62–63 meters, consisting of thinly laminated marl rich with clay named varvites. Varvites or laminites, as defined by KOCHANSKY (1944), are interchangeable layers of light marl with calcite and dark marl with organic matter ("Tripoli" sediments).

Among the first mineralogical research done on the Kostanjek landslide site was by BALEN et al. (1975) using microscope analyses. Among their samples, they differentiated two structures: homogenous marl, corresponding with the Lower Panonian unit, and marl with white and grey alternating layers, corresponding with the Sarmatian thinly layered clays. In the latter unit, the white layers were identified as a carbonate component, while the grey layers were rich with clay minerals.

In SLOVENEC (1989), the Sarmatian unit was further researched. The alternating white and grey layers were attributed to the Tripoli Fm. in accordance with the abundance of diatomite and radiolarian fragments. Both the white and grey components were determined as containing a large amount of amorphous SiO_2 and organic matter. The white component contained mostly aragonite, with a smaller amount of calcite, gypsum and a minor amount of clay minerals, while the grey component consisted also of aragonite and calcite, along with dolomite and less amorphous matter than the white, but more organic matter and irregularly interstratified phyllosilicate minerals. The phyllosilicates identified were montmorillonite (15–20 %) and chlorite, while samples from the Upper Sarmatian showed a significant presence of micaceous minerals.

Mineralogical analysis by X-Ray diffraction was done by MARTINČEVIĆ et al. (2013) on samples from the B-1 borehole in the mid-part of the landslide area. Four stratigraphic units were differentiated: Quaternary soils, Upper Panonian massive marl, Lower Panonian marl and Samatian laminated clays. Clay minerals were the main component in all units except one, the Lower Panonian, where they are present in the same amount as calcite. The amount of calcite generally increases with depth. The clay minerals determined in these samples were smectite with 50–70 wt% throughout the analyzed interval, along with kaolinite, chlorite, illite and muscovite (Fig. 8). In MARTINČEVIĆ LAZAR et al. (2013), the mineralogical composition of these samples was confirmed, along with the presence of a calcite component. They refer to the fact that, along with sliding, the Kostanjek Landslide area had been experiencing settlement and sinking which can be linked to swelling processes.

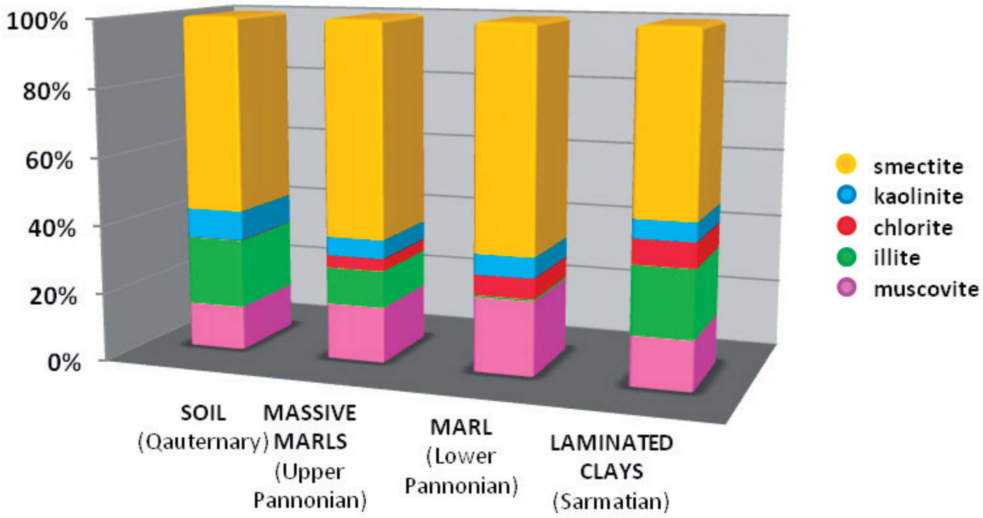

Figure 8. Prorportion of clay minerals in each sedimentary unit (MARTINČEVIĆ et al., 2013).

In ŠTIMAC (2016), an interval of Upper (59.03 m – 62.95 m) and Middle Sarmatian samples (63.40 m – 63.51 m) from the B-1 borehole were analyzed, keeping in mind the depth of the slip surface previously identified by KRKAČ (2015). The Upper Sarmatian samples consisted of smectite, illite, kaolinite (both well and poorly ordered) and chlorite, while the Middle Sarmatian samples showed presence of dominantly mixed-layered clays (Fig. 9). The first decline in clay mineral content happens in the Upper Sarmatian unit at 62.75 meters, then increasing before decreasing again in the Middle Sarmatian. Another significant difference was the content of carbonate minerals, where the amount of aragonite increased significantly in the Middle Sarmatian samples - up to 66 wt% as opposed to as low as 11 wt% in the Upper Sarmatian. The dominant cation in the Upper Sarmatian samples was estimated as Ca, possibly as a consequence of carbonate dissolution, with Na assuming this role in the Middle Sarmatian, increasing the tendency of chemical bond breaking.

All of the above, indicating a change in mineral content on and around the boundary of two Sarmatian lithostratigraphic units, and especially the presence of mixed-layered clays that include smectite layers, holds the possibility of a negative effect on the engineering properties of these sediments and the activation of the sliding process.

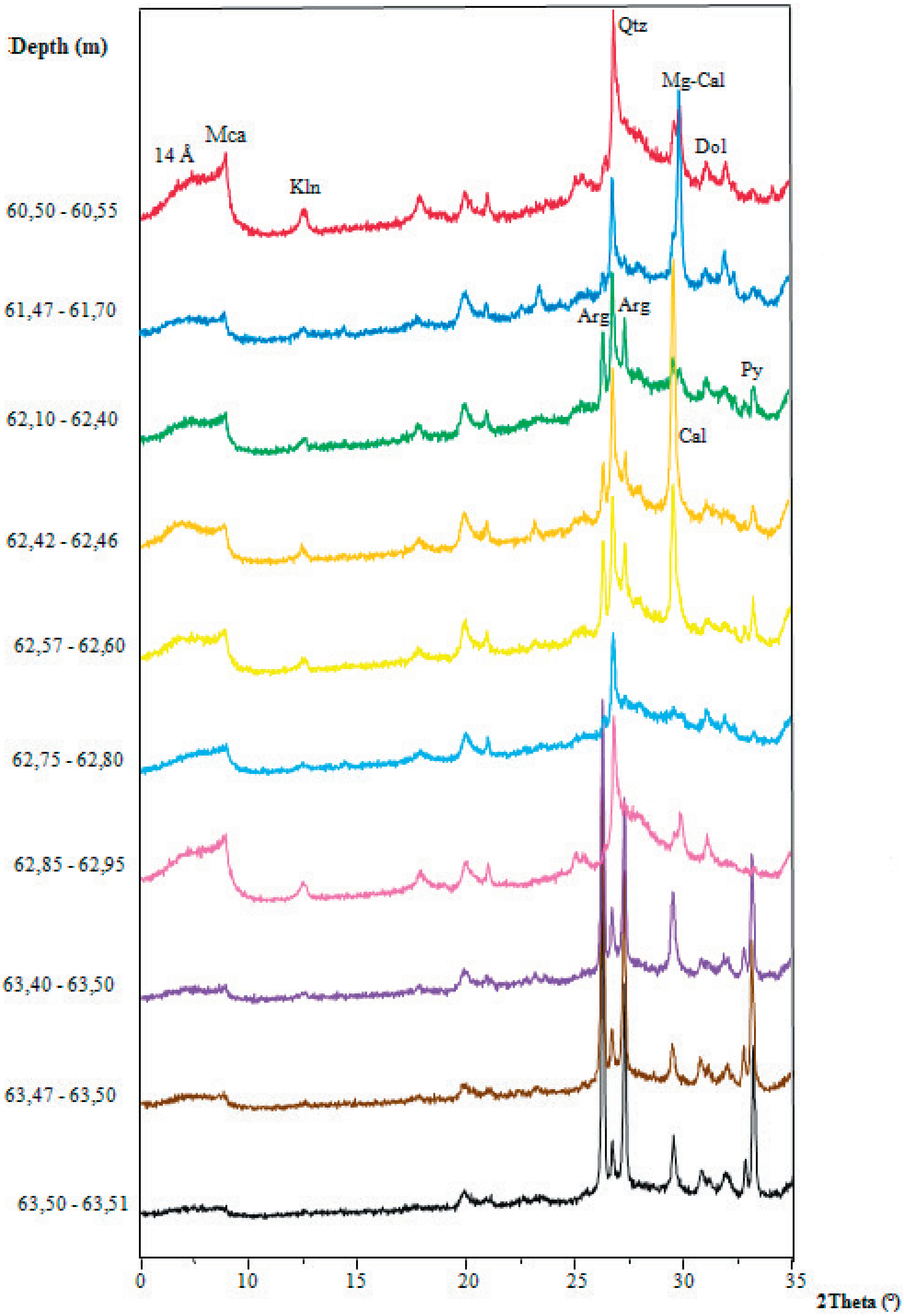

Figure 9. Difractograms of the <2μm fraction by depth (ŠTIMAC, 2016). Key: Mca – micaeous minerals; 14 Å – minerals with 14 Å diffraction maximum (smectite,vermiculite, chlorite); Kln – kaolinite; Qtz – quartz, Cal – calcite, Mg-Cal – magnesium calcite, Dol – dolomite, Py – pyrite, Arg – aragonite. Note: micaeous minerals include muscovite, illitic material and mixed-layer illite-smectite

STOP 2: Zeolitized pyroclastics of the Donje Jesenje

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Pyroclastic rocks that occur in abandoned quarry near Donje Jesenje are 52 m thick. They are of Early Miocene age and belong to the Vučji Jarek Mb. of the Macelj Fm. (ŠIMUNIĆ, AN. et al., 1995; AVANIĆ, 2012). Tuff was first exploited as ornamental construction stone, but this stopped due to its inadequate application in exterior, latter for the cement industry as pozzolanic material, and lately as zeolite raw material. Natural zeolites due to their abundance and low cost have widespread application in environmental protection and remediation, in agriculture for soil treatment, as pet litter, ad additive in animal nutrition, for construction materials etc.

Description: Pyroclastics are laterally correlative with the upper part of deposits of the facies of horizontally and cross-bedded glauconitic sandstones which are observable at Stop 3. The deposits are mostly horizontally bedded, with the bed thickness which usually varies between 1 and 30 cm (Fig. 10). Some beds are thicker reaching the thickness up to 5 m. Trough cross-bedded pyroclastisc of sandy grain-size occur just in a few beds.

Figure 10. Facies of horizontally and cross-bedded pyroclastics (photo by R. Avanić).

Tuffs prevail in the pyroclastics. They show vertical alternation of vitroclastic, vitrocrystalloclastic, crystalloclastic and crystallolithoclastic types (GOLUB & BRAJDIĆ, 1969; ŠIMUNIĆ, AL. et al., 1988). Pumice characterized by hollows that are irregularly dispersed or parallel to the bedding plane occurs within the pyroclastics. The hollows are empty or are infilled by clayish material produced by devitrification of volcanic glass (Fig. 11). Volcaniclastic rocks have variable primary composition, the main constituents of vitroclastic and crystalloclastic tuffsare volcanic glass, plagioclase feldspars (andesine) and biotite, while amphibole and quartz occur seldomly. Lithoclastic tuffs are composed of tuff and effusive rocks fragments, and in smaller quantities mineral fragments and glass. In the quarry SiO_2 content varies between 65 and 70 %, therefore tuff was determined as dacitoandesitic. The rocks contain various alteration products of volcanic glass (Fig. 12). The alteration products comprise zeolites, clay minerals (smectite, authigenic mica), SiO_2 phases and authigenic feldspars (TIBLJAŠ, 1996; TIBLJAŠ & ŠĆAVNIČAR, 2007). Clinoptilolite (based on the Si/Al ratio) is the most abundant zeolite, however analcime and mordenite are also present. The type of exchangeable cations in clinoptilolite is variable; therefore clinoptilolites were divided into three subgroups: Ca-, Ca-K-, and Na-rich.

Clinoptilolite content in the volcaniclastic rocks discovered in Macelj area vary significantly, in some rocks it is the dominant component, in others it is present only in traces. In Donje Jesenje quarry, in which due to exploitation the best outcrops of these rocks can be found, the variations, although present, are not so conspicuous, and the average content of clinoptilolite is approximately 50 wt.%.

Authigenic mica occurs in thin veins (Fig. 13) and coatings, made of laths, of glass shard vesicles (Fig. 14). X-ray powder pattern with widened but still relatively sharp reflections is characteristic for 1M micas, with Fe-rich octahedral sheet. The observed $d_{(060)}$ value is 1.508 Å. IR spectrum is characterized by sharp absorption bands in the OH stretching region, with two strongest bands at 3580 and $3600 cm^{-1}$ ascribed to $Al\text{-}Fe^{3+}$ and Al-Mg cationic environment of the OH groups. Microprobe analyses revealed that this is an interlayer-deficient dioctahedral mica, with Al as dominant cation in octahedral sheet, $^{VI}M^{3+}>1.2$, and low tetrahedral substitution (TIBLJAŠ et al., 2004), with quite peculiar chemical composition that does not correspond ideally to any member of the mica group as defined by RIEDER et al. (1998). It can be best classified as interlayer-deficient alumino-celadonite.

Figure 11. Dark clasts of devitrified pumice fragments in pyroclastics as an indicator of the synsedimentary explosive volcanic activity (photo by R. Avanić).

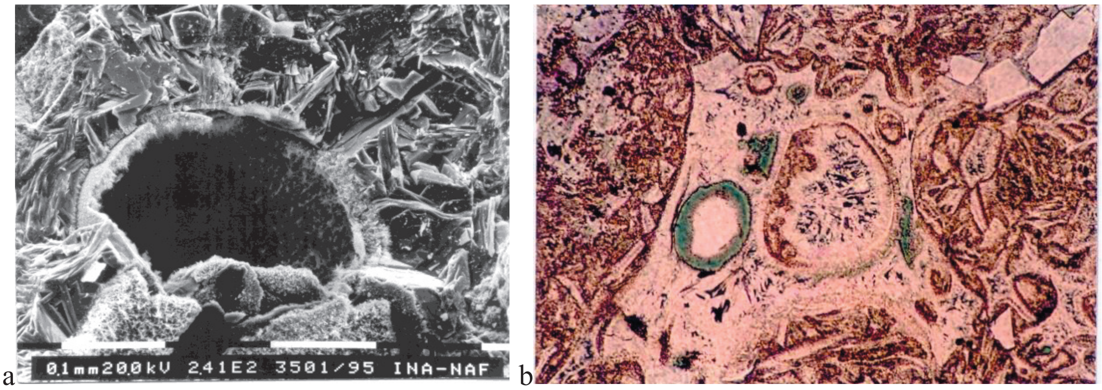

Figure 12. SEM microphotograph of volcanic glass shard altered to platy clinoptilolite. Vesicle within the shard is lined by laths of authigenic mica (photo by R. Slavković) (a); Microphotograph of tuff from Donje Jesenje quarry showing glass shard altered to platy clinoptiloite and authigenic mica (celadonite) present as lining of vesicle (diameter of the vesicle is ca. 0.1 mm) TIBLJAŠ et al. (2004) (b).

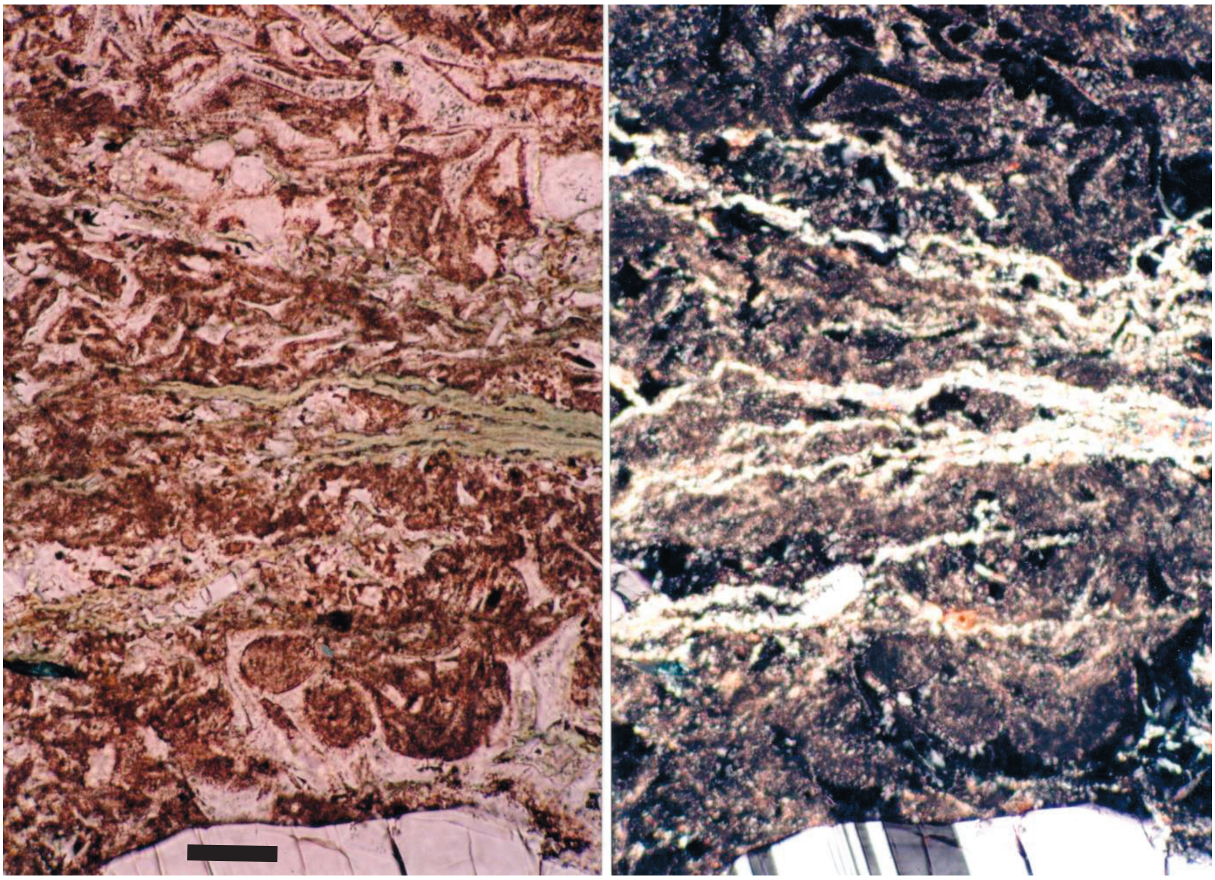

Figure 13. Photomicrograph of veinlet filled with green mica mineral in tuff containing glass shards, altered to clinoptilolite, and plagioclase phenocrysts in fine grained matrix. Black line is 0.1 mm. right - plane-polarized light; left - cross-polarized light – due to second order interference colours veins with authigenic mica are clearly visible TIBLJAŠ et al. (2004).

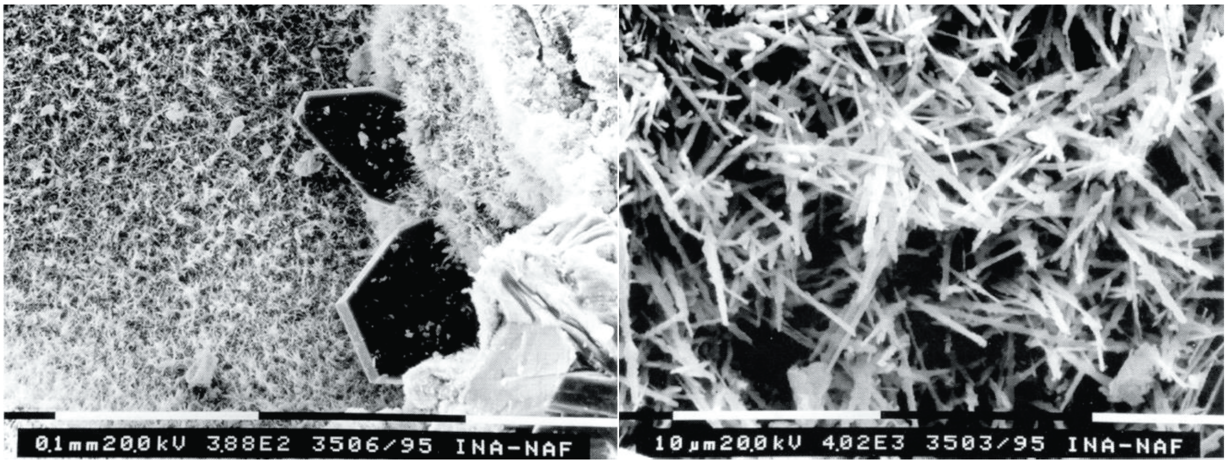

Figure 14. SEM microphotograph showing two platy crystals of clinoptilolite within vesicle of altered volcanic glass shard in tuff from Donje Jesenje quarry. The surface of the vesicle is lined by laths of authigenic mica (right); Higher magnification SEM microphotograph of authigenic mica laths (app. 0.1x0.25x10 µm) (left) TIBLJAŠ et al. (2004).

In the upper part of the succession chaotic pyroclastics showing slumping occur (Fig. 15). They consist of tuffs with dispersed fragments of lapilli composed of volcanic glass, lithoclasts and crystalloclasts. The lithoclasts are composed of andesite or tuff. Rounded tuff blocks up to 5m in diameter occur rarely (Fig. 15). The uppermost part of the succession is characterized by tuffs that are strongly affected by modern weathering processes that resulted in alteration into a sandy material.

Figure 15. Chaotic pyroclastics indicate the proximity of the volcano (photo by R. Avanić).

Interpretation: Pyroclastics were probably deposited in a marine environment as indicated by pumice with hollows formed parallel to bedding planes that reflects rapid cooling of volcanic ash in water, and relatively quick settling on the bottom (WHITHAM & SPARKS, 1986; McPHIE et al., 1993; CAS & WRIGHT, 1995). The interpretation is supported by cross-bedded pyroclastics that suggests subaqueous dune migration by currents in a shallow marine environment (ASHLEY, 1990). Chaotic pyroclastic in the upper part of the succession are interpreted as a result of density flows generated by seismic shocks caused liquefaction and destabilization of pyroclastic material produced by submarine eruptions (sensu CAS & WRIGHT, 1995). The thickness of pyroclastics indicates a relatively long-lasting explosive volcanic activity. The activity was characterized by changeable intensity. The high intensity produced crystalloclastic tuff and high accumulation of pumice, while the low intensity resulted in vitroclastic tuff and low accumulation of pumice (ŠIMUNIĆ, AL. et al., 1988; McPHIE et al., 1993).

Alteration of volcanic glass is the result of burial diagenesis. Different alteration products are most probably due to different temperatures to which sediments were exposed, with increasing depth of burial clinoptilolite transformed to mordenite and analcime, while opal-CT changed to opal-C and recrystallized to quartz. However different immobile element content of rocks containing different alteration products indicates that alteration was probably also dependent on chemical composition of the rocks. It seems that sometimes type of alteration product was also dependent on primary material granulometric characteristics. Huge reserves of volcanoclastic rocks make them economically interesting, nevertheless it will be necessary to take care about raw material properties i.e. zeolite content and its chemical composition, when planning its particular application.

In the area, bentonite deposits have also been investigated around Bednja; the exploitable amounts were found in Šeprun and Šaša. These deposits were formed by alteration of vitroclastic tuff and volcanic glass of Early Miocene age (MARKOVIĆ, S, 2002). The immobile microelement composition suggests felsic to intermediate volcanism.

The clay pit in Šaša was active, although not continuosly, from 1926 when surface excavation started, until 1990s when the reserves were depleted. Bentonites from Šaša were used in castings, as its quality was deemed unsuitable to be used in drilling fluids. The deposit is 10 to 35 m thick, plate-shaped, placed within the layer of coarse-grained arenites of Early Miocene (BRAUN, 1991).

The dominant mineral is a high-charge montmorillonite with a high Fe-content. The main interlayer cation is Na. Other minerals present include plagioclase, quartz, opal-CT and trace amounts of kaolinite, calcite and zeolite from the heulandite-clinoptilolite series. XRD data showed some degree of interstratification with 10-20% of illite layers. The CEC values have been determined at 85 meq/100g.

STOP 3: Glauconitic sandstones of the Vučji Jarek

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Lower Miocene glauconitic sandstones, and glauconitic material within it, occurring in the Macelj area were previously investigated by many authors: GORJANOVIĆ-KRAMBERGER (1904a, 1904b), TIŠLJAR & ŠIMUNIĆ, AL. (1978), ŠIMUNIĆ, AL. et al. (1988, 1990), PROHIĆ (1988), ŠIMUNIĆ, AN. et al (1995), SLOVENEC et al. (1997), TADEJ et al. (1997), ALJINOVIĆ et al. (2003), AVANIĆ et al. (2005, 2015), TIBLJAŠ et al. (2006).

In the area of Macelj ŠIMUNIĆ, AN. et al. (1995) described the lithostratigraphic Macelj Fm. The lithostratigraphic unit Macelj consists of 4 members: Vučji Jarek, Čemernica, Lipni Vrh and Vrbno (AVANIĆ, 2012) (Fig. 3). Vučji Jarek Mb. is represented by horizontally and cross bedded glauconitic sandstones of Eggenburgian age (Early Miocene, AVANIĆ et al., 2005).

Description: Glauconitic sandstones are up to 138 m thick. Deposits of horizontally bedded sands are in the base of the glauconitic sandsones which are overlain by deposits of structureless clayey-silty sands. The contacts between the facies are not visible. Horizontally bedded sandstones predominate over cross-bedded sandstones in the facies. The thickness of horizontally bedded sandstones varies between 1 and 20 cm. The cross-bedding shows the planar and through type. The planar cross-bedding forms sets about 0.1–3.5 m thick, while the through cross-bedded sets are between 0.5 and 1.5 m thick. Individual throughs within the sets are up to 12 m wide. Boundles composed of sandstone-mud coupplets with varying thickness occur on places (Fig. 16). Sets are separated by horizontally bedded and laminated sandstones which in some places show asymmetric cross-lamination. Herringbone cross-stratification also occurs in the facies (Fig. 17). Measurements of the paleotransport and detailed geological mapping indicate that the transport direction was between northwest and northeast.

Figure 16. Contact of planar cross-bedded sandstone-boundles (over hammer) and sandstones with horizontal laminations and little current ripples laminations (in the hammer level). Detail of the facies of horizontally cross-bedded glauconitic sandstones on the Vučji Jarek column (photo by R. Avanić).

Figure 17. Herringbone cross-bedding in the facies of horizontally and cross-bedded glauconitnic sandstones (Locality Osredečki) (photo by R. Avanić).

Figure 18. Thin section showing glauconitic pseudomatrix in sandstones of Vučji Jarek Mb. (photo by M. Belak).

Sandstones are fine to medium grained and well sorted. They are greyish to greenish in colour due to the present glauconite (Fig. 18.) The glauconite is highly accumulated in some laminae. The glauconite grains are often kidney-shaped with cryptocristalline to microcristalline or sometimes platy structure. Beside the glauconite, quartz, lithic particles and feldspars prevail in the sandstone, while chlorite, muscovite and biotite occur rarely (ŠIMUNIĆ, AL. et al., 1988). The feldspars are represented by microcline, oligoclase and andesine. The lithic particles are represented by metamorphic rock fragments (quartzite, and quartz, mica, sericite and chlorite schists), altered volcanics, felsic intrusives (granite and pegmatite), tuffs, cherts, carbonates and shales (ŠIMUNIĆ, AL. et al., 1990). The carbonate particles are composed of dolomite and skeletal fragments of marine organisms. Translucent minerals prevail within the heavy mineral fraction. They are represented by tourmaline, zircon, apatite, staurolite, routile, epidote and amphibole. The sandstone is cemented by a mixture of quartz, dolomite and calcite while matrix occurs rarely (ŠIMUNIĆ, AL. et al., 1990). The sandstones are determined as glauconitic lithic arenites, graywackes and glauconitic graywackes (ŠIMUNIĆ, AN. et al., 1995).

In these sediments pectenid shells were determined, among others species: *Chlamys northamptoni* var. *oblita* MICHELOTTI, *C. macrotis* (SOWERBI), *C.* cf. *darnóensis* Csepreghy, *C.* ex gr. *holgeri* (Geintz), *Flabellipecten* ex gr. *burdigalensis* (LAMARCK) *Pecten* sp., *P. psudobeudanti* Deprét et RomaN, *Gastrena vragilis* var. *gracilis* SHAFFER (ŠIKIĆ, K., 1991, 2004; ŠIMUNIĆ, AN. et al., 1995). Based on these marine macro-fossils these sediments were determined as Eggenburgian (ŠIKIĆ, K., 1991, 2004). This age was confirmed by K-Ar dating method (19.21 ± 0.64 Ma - AVANIĆ et al., 2005).

Interpretation: The fossil association and glauconite grains documents a shallow marine environment while the planar and trough cross-bedding suggest deposition by traction, probably by 2D and 3D subaqueous bedforms. The 1.5 m thick troughs indicate migration of large dunes by strong currents (ASHLEY, 1990). The bipolar palaeotransport and bundles composed of sandstone-mud couplets, and herringbone cross-bedding indicate deposition by reverse currents that suggests a tidal environment (PHILLIPS, 1984; DALRYMPLE, 1994; JOHNSON & BALDWIN, 1996), as was interpreted earlier (ŠIMUNIĆ, AL. et al., 1988, 1990; AVANIĆ et al., 2005; AVANIĆ, 2012). Similar to horizontally bedded sands, the composition and thickness of glauconite sandstones indicate a strong terrestrial influence and tidal deposition during a long period.

The palaeotransport directions indicate prevailing currents towards between NW and NE in the tidal environment. They are documented by the planar cross-bedding, and bundles composed of sandstone-mud coupplets, where the mud represents opposite weak currents. Such bundles usually occur in estuaries, tidal channels, and on the shelf with strong tides. Since documents which indicate estuarine or tidal channel deposition, such as fossil or gravel lag, were not found at the Vučji Jarek locality, deposits of glauconite sandstones probably belong to the nearshore or shallow shelf (EINSELE, 1992; DALRYMPLE, 1994; READING & COLLINSON, 1996; JOHNSON & BALDWIN, 1996).

Glauconitic material: Glauconitic material is present in several members of Macelj Fm. Those separated (Fig. 19) from the lowermost member (Vučji Jarek), deposited within a marine, nearshore environment under tidal influence, and the overlaying Čemernica Mb., formed in the offshore-transition zone between shoreface and offshore, were investigated by X-ray powder diffraction (XRPD), infrared (IR) and Mössbauer spectroscopy, and by chemical methods (TIBLJAŠ et al., 2006).

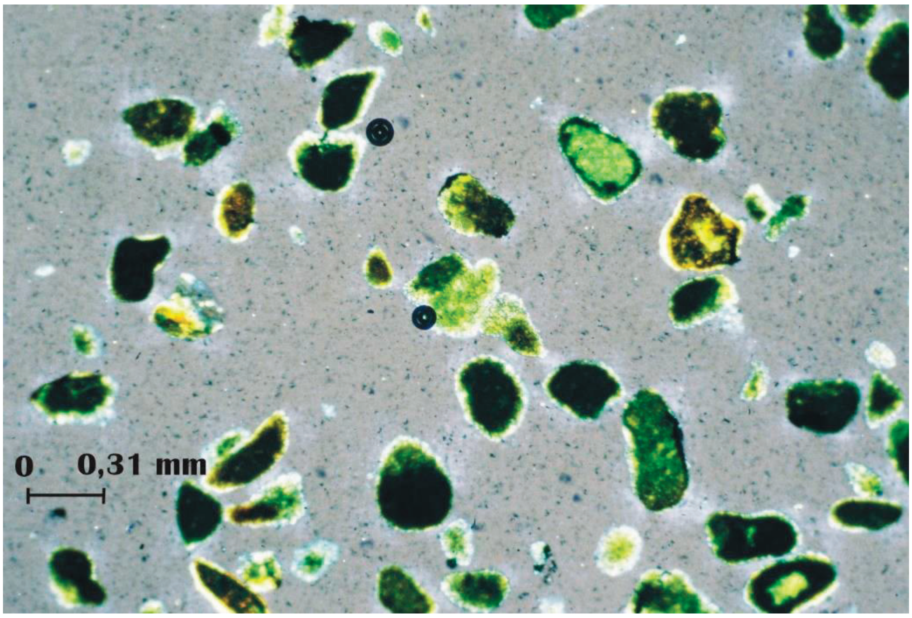

Figure 19. Grains of glauconitic material separated from Vučji Jarek sample, crossed polarizers (photo by M. Belak).

Investigated glauconitic materials from two members differ significantly. XRPD patterns showed no impurities in investigated materials (Fig. 20). Diffraction patterns of Čemernica samples have broader diffraction maxima, this is best seen for 001 peak, indicating higher expandable layer content. The observed $d_{(060)}$ for these samples of 1.511 Å in comparison to 1.516 Å for Vučji Jarek samples indicates higher Al content in them. In spite of the fact that IR spectra of all samples are characterized by poorly resolved broadened bends, they differ in the appearance of the OH-stretching region. Those from Čemernica Mb. samples have more pronounced bands at 3603 and 3625 cm^{-1}, which can be ascribed to Al-Mg and Al-Al cationic environments of the OH groups respectively (BESSON & DRITS, 1997) in addition to bands at 3557 (Mg-Fe^{3+} and Al-Fe^{2+}) and 3530 cm^{-1} (Fe^{3+}-Fe^{3+}) that are practically the only visible bands in Vučji Jarek samples. In two samples from the Vučji Jarek sediments potassium content (7.75 and 8.03 wt% K_2O) was higher than in two samples from Čemernica Mb. having 5.58 and 6.24 wt% K_2O respectively, what is in accordance with observed differences in XRPD patterns. Therefore, according to division of ODIN & FULLAGAR (1988) glauconitic materials from the Vučji Jarek Mb. are evolved while those from the younger Čemernica Mb. are slightly-evolved to evolved. The content of expandable layers in Vučji Jarek and Čemernica samples is, according to relation given by VELDE & ODIN (1975), approximately 5 and 20 % respectively. Mössbauer spectra recorded at room temperature show differences for samples belonging to different members and were therefore fitted with different number of doublets with Lorentzian line shape. In accordance with DRITS et al. (1997) differences were presumed to be a result of different sets of local cation arrangement around Fe^{3+} and different Fe^{3+}/Fe^{2+} ratios. Fitting of Čemernica Mb. samples spectra with four quadropole doublets of Fe^{3+} again indicate their higher Al content.

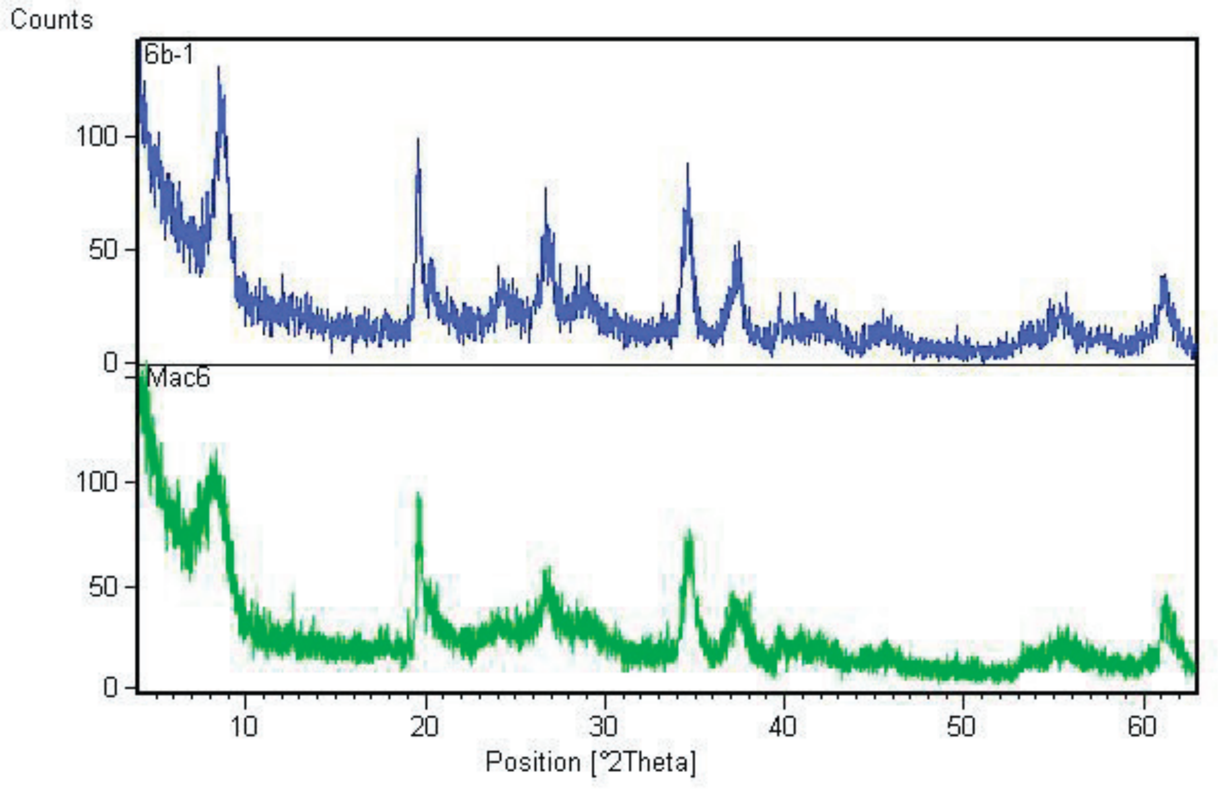

Figure 20. XRPD patterns of samples 6b/1 from Vučji Jarek Mb. and Mac6 from Čemernica Mb.

STOP 4: Trakošćan Castle and bedded conglomerates and sandstones of Trakošćan

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Trakošćan Castle

Trakošćan Castle (Fig. 21), one of the most attractive castles in Croatia, together with its lake and forest park is "hidden" in the picturesque north-western part of Hrvatsko Zagorje in the region formed by Maceljska Gora (715 m) and Ravna Gora (680) Mts. It is located in a strategic position on the road from Ptuj to Bednja valley on the hill made from resistant conglomerates and sandstones. It is assumed that it dates back to the 13th century, and that it served as a small observation fortress, although the first written mention of the toponym "Trakošćan" (Tracustian) is dated to 1334. Prior to 1569, when it was given by decree of king Maximillian II to the Croatian Ban and the Bishop of Zagreb Juraj II Drašković, it was ruled by several owners. After that, it was almost continuously in the possession of Drašković family till 1944. It was nationalized in 1945, and in 1953 the Museum of Trakošćan was established. At first it was built as Romanesque fort, but during time due to invention of firearms and the growing threat of Turkish attacks it was extended and further fortified. At the turn of the 19th century the fort lost its defensive role and its owners abandoned and neglected it. In the period 1840–1862 Count Juraj VI Drašković transformed the ruins into the luxurious Neo-Gothic castle-summer residence. Today the castle contains the elements of Gothic architecture dating back to 14th century, Renaissance and Baroque features from 16–18th centuries together with Neo-Gothic ones from the 19th century. Almost six meters high dam built bellow the castle, in the time of his restoration, transformed a swampy valley of Čemernica brook into an artificial lake, and the castle surroundings were designed as an English kind of park (HABRUN, 2012).

Figure 21. Trakošćan Castle (photo by D. Tibljaš).

Conglomerates and sandstones of Trakošćan

The bedded conglomerates and sandstones are located at the base of the southwest side of the Trakošćan Castle. These sedimentary rocks form a natural hillock exploited by the builders for the fortification purposes (Fig. 22). Deposited during the Eggenburgian (the Early Miocene) they are the part of the Lipni Vrh Mb. of the Macelj Fm. (AVANIĆ, 2012; AVANIĆ et al., 2015).

Figure 22. The walls of the Trakošćan Castle built on natural foundations composed of bedded conglomerates and sandstones (photo by R. Avanić).

A number of geologists have researched these deposits on the territory of Hrvatsko Zagorje. BOJANIĆ et al. (1978) described Miocene sandstones and conglomerates which, save for the dimension of grains, differed also according to respective quantities of lithic particles and volcaniclastic material. TIŠLJAR & ŠIMUNIĆ (1978) determined "Macelj sandstones" along the road Macelj-Trakošćan as lithoarenite and tuffitic sandstones in alteration with conglomerates, tuffs, clays and clayey marls. ANIČIĆ & JURIŠA (1984; 1985) in the area of Maceljska Gora Mt. and hillsides of the Ravna Gora Mt. distinguished quartz sands, sandstones, conglomerates and sandy clays of the Burdigalian (Eggenburgian) age. ŠIMUNIĆ, AN. et al. (1995) presented the main lithostratigraphic members of the Lower Miocene of the north-western part of Hrvatsko Zagorje and explained, in addition to the Vučji Jarek and Čemernica Mbs., the main lithologic, stratigraphic and ecologic characteristics of the deposits of the Lipni Vrh Mb. from the Macelj Fm. AVANIĆ (2012) provided a detailed description of the facies of bedded conglomerates and sandstones as well as correlations with other facies of the Macelj Fm. in the broader evolutionary context of the sedimentary basins in the Early Miocene of Hrvatsko Zagorje.

Description: Geologic cross-section of the Trakošćan bedded conglomerates and sandstones contains in its lower portion fine-grained conglomerates (Fig. 23) overlain by 7 m thick cross-beds of coarse-grained to granulated, more rarely fine-grained sandstones (Fig. 24). Since characteristics of cross beds are hard to define due to the covering, palaeotransport also remains undefined. However, above the cross-section, at the base of the Trakošćan Castle one can observe cross-beding indicating possible palaeotransport toward the north-east. Conglomerates are fine-grained, either framework-supported or matrix-supported. Matrix is medium-grained to coarse-grained sandstone (lithoarenite). The grain size ranges between 0.2 and 1.0 cm, and rarely up to 4.0 cm in diameter. The pebbles are composed of cherts, quartz, quartzite, silicified tuff, dolomite, quartz- and chlorite-sericite schist, granite, vitric tuff, tuffite and siltite, and, more rarely, fragments of fossils (ŠIMUNIĆ, AL. et al., 1990). The quartzite pebbles are medium- to well-rounded while those made of tuff, tuffite and siltite are angled or poorly-rounded. Sandstones are coarse-grained (assuming conglomerate habitus) to fine-grained, medium to well sorted. The component parts are half-angled, half-rounded to round. The detritus of sandstone samples includes quartz, feldspars, rock fragments, and glauconite (ŠIMUNIĆ, AL. et al., 1990). The grain composition is similar to conglomerates (cherts, quartz, quartzite, silicified tuff, dolomite, quartz- and chlorite-sericite schist, granite, vitric tuff, tuffite and siltite). Dolomite, siderite, limonite and quartz cement predominates. Sedimentary rocks have been determined as micaceous lithic arenites and sub-lithic arenites with minor glauconite (ŠIMUNIĆ, AN. et al., 1995). Sparse micro- and macro fauna of the "Facies of bedded conglomerates and sandstones" of a broader area indicates the probable Miocene age. However, thanks to the known age of underlying and overlying strata the bedded conglomerates and sandstones can be said of to positively apply to the Eggenburgian.

Figure 23. Fine-grained conglomerates in the lower part of the cross-section of the "bedded conglomerates and sandstones of Trakošćan" (photo by R. Avanić).

Figure 24. The cross-bedded sandstones at the cross-section of the "bedded conglomerates and sandstones of Trakošćan" (photo by R. Avanić).

Fossil detritus indicates that the bedded conglomerates and sandstones were deposited in the marine environment. Fossil detritus, the grain and pebble size as well as cross-bedding suggest the high energy of water. Coarse-grained (conglomerate) to fine-grained sandstone with units of characterized by cross-bedding could well represent cross-bedded sands from the shelf of the delta mouth. Since the measuring of the third dimension of individual textures with purpose of spatial delineation of the sedimentary bodies was unfeasible at the cross-section deposition of these sedimentary rocks in the marine coastal environment, with input of high quantities of terrigenous material of generally deltaic characteristics, was only suggested.

STOP 5: Krapina Neanderthal Museum and Site Hušnjakovo

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In the heart of the Hrvatsko Zagorje, in the small, but important cultural and historical town of Krapina, the Neanderthal site – Hušnjakovo is situated. The story of the Krapina early men discovery began quite accidentally, at the end of the 19th century, when the inhabitants of Krapina exploited the sand on Hušnjakovo hill for construction purposes. Many unknown and strange fossil bones were found on the field, and some of them were collected by Josip Rehorić, the Krapina geography teacher, and sent them by mail to Dragutin Gorjanović-Kramberger, who was Director of the Geological and Palaeontological Department of the National Museum and professor of palaeontology and geology at the University of Zagreb. Gorjanović-Kramberger came for the first time in Krapina on August 23, 1899 by the invitation of Mayor Vilibaldo Sluga to study strange finds at the bottom of Hušnjakovo Hill, near Kneipp Spa (Fig. 25). With more detailed analysis of the yellow Miocene sandstone deposits, about 8 meters high, Gorjanović saw the ash and stingy sand, stone tools and remains of animal bones, but human molar gave him a definite confirmation that Hušnjakovo was place of ancient human habitat. In systematic excavations and research that lasted from 1899 to 1905, Dragutin Gorjanović-Kramberger collected about 900 human fossil remains of about 70 individuals of different ages and gender, making the Hušnjakovo site, place with the largest single collection of Neanderthals in the world. The average age of Neanderthals according to fossil bones was 13 to 14 years, while the oldest was about 27 years old. Beside the human fossil bones, Gorjanović-Kramberger collected about 1,200 pieces of stone tools (Musterian type) and over 2,300 animal bones: cave bear, wolf, elk, giant deer, woolly rhinoceros, wild buffalo, leopard etc. Neanderthals also used fire. Burned bones are proof of controlled fire and roasted meat. Dragutin Gorjanović-Kramberger published results of his research in two monographs "Diluvian man from Krapina" (1906) and "The life and culture of the diluvian man from Krapina in Croatia" (1913).

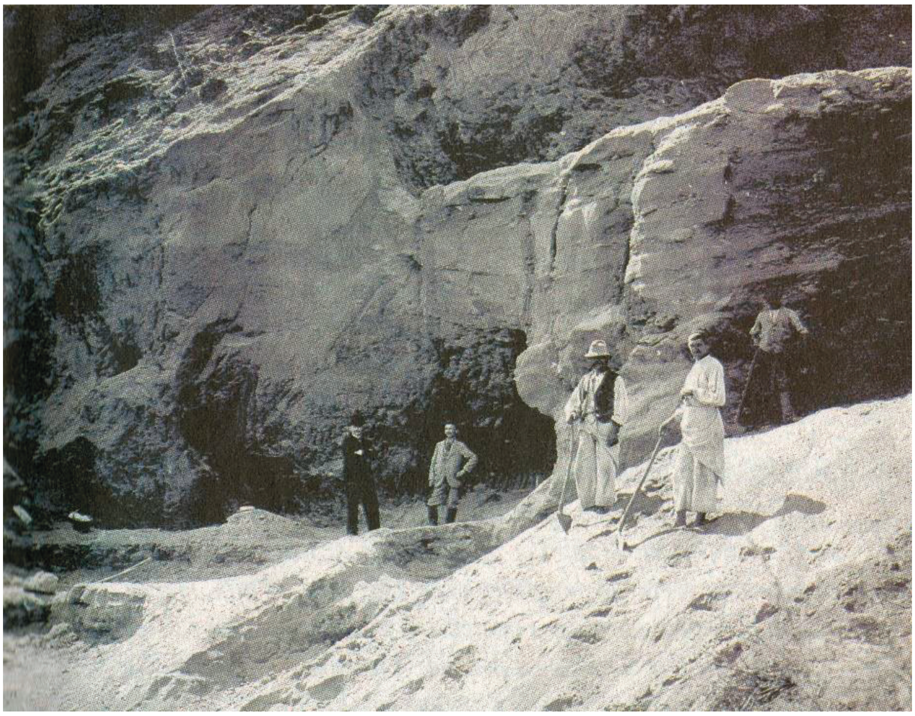

Figure 25. The beginnings of investigations at the Hušnjakovo site in 1899 (photo from the Krapina Neanderthal Museum Archives).

There are about three hundred skull and jaw bones in Krapina collection and nearly four hundred bones of other body parts. In addition to the famous skulls, skull bones are also represented by remains of forehead, head and neck bones, and hearing bones. The other remains in the collection are: 61 vertebrae, 56 ribs, 22 blades, 15 clavicle, 21 bones of upper arm, 30 forearm and 58 bone hands. There are also pelvic bones, thigh bones, knee-bone and bones of the foot. Krapina's findings tell us about the Neanderthal morphology: muscular texture, shorter but stronger limbs, strong joints, bony shape of the chest, lower growth, stronger forehead bone, croup and short forehead, bigger teeth, flat chin, straight and elongated vertebrae, large volume brain. Although, there is no single complete skeleton in collection, the bones are well preserved, but are very fragile and fragmented and are not suitable for genetic research. In 1995, the ESR (Electron Spin Resonance) method, used for the analysis of the dental enamel of the wooly rhinoceros, assessed the age of the Krapina prehistoric findings to about 125,000 years. Krapina Neanderthals lived in the period of the last great Middle Ages of Riss - Würm and are counted among the older Neanderthals of Europe. Scientific research and professional processing of the collection, which lasts for almost 120 years, is constantly coming up with new discoveries and data. Osteological analyzes found the earliest cuts of the right forearm amputation, healing of severe head injuries and recovery from the coma. Frequent bone disorders such as arthritis, osteopenia, periostitis, sclerosis, and bone cancer are evidence of the severe and very stressful life of the first inhabitants of Krapina. The most important finding of the Krapina collection is Krapina 3 or skull C - skull belonging to young, mature Neanderthal woman. This finding is interesting because of the thin and shallow cutmarks (in total 42) found on the fore part of the skull pointing to the possible ritual behavior of Neanderthals (Fig. 26). Recent research of the eagle claws from the Krapina collection revealed that Neanderthals were making jewels, suggesting that Neanderthals had the capability for a much more complex, symbolic way of thinking than it was considered before.

Figure 26. Skul Krapina (photo by L. Mjeda).

Knowledge of Krapina early man are presented in the permanent exhibition of the Krapina Neanderthal Museum (Fig. 27), which, along with numerous castings and copies of findings and multimedia installations, also contains reconstructions that are part of the largest diorama of the Neanderthal man (Fig. 28) in the world. The permanent exhibition of the Museum is a kind of time machine (Fig. 29) that leads visitors from the oldest past of the Earth to the modern times, emphasizing the significance of the Krapina Neanderthals and the place of its discovery. Site Hušnjakovo is the first protected paleontological monument of nature in Croatia in 1948. The Krapina Neanderthal Museum has around 90,000 visitors per year and is one of the most visited museums in Croatia and in this part of Europe. The world importance of this unique site has been confirmed by the European Commission, awarding the European Heritage Label to the Site and Museum in March 2016.

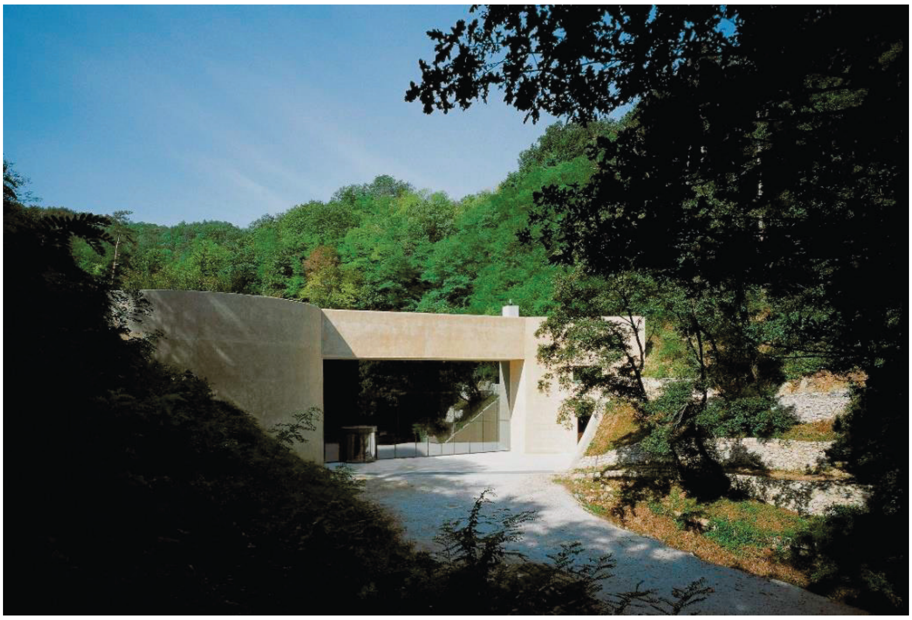

Figure 27. Krapina Neanderthal Museum (photo by D. Fabijanić).

Figure 28. The largest diorama of the Neanderthal man in the world (photo by E. Daynès).

Figure 29. Permanent exibition (photo by D. Fabijanić).

Acknowledgments

The organizers are grateful to Marko Budić, Miroslav Kladnički and Tomislav Kurečić for help in preparation of the maps in the Field Trip Guide Book. Special thanks go to Jesenje Municipality Mayor Andrija Ranogajec and the Public Institution for management of protected natural areas of Krapina-Zagorje County for the help in organization of the field trip.

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