MECC14

7th MID-EUROPEAN CLAY CONFERENCE 2014

16–19 SEPTEMBER 2014 • DRESDEN • GERMANY

www.mecc2014.de

PROGRAMME AND ABSTRACTBOOK

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Table of Contents

General Information

Scientific Programme

Organisation and Imprint

Conference Organiser

Deutsche Ton- und Tonmineralgruppe e. V. (DTTG)

Conference Website

www.mecc2014.de

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Michael Plötze (Zurich/CH)
Helge Stanjek (Aachen/DE)

Representative of the National Clay Groups

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Miroslav Pospisil (Czech Republic)
Marta Mileusnic (Croatia)
Helge Stanjek (Germany, Austria and Switzerland)
Michal Skiba (Poland)
Istvan Dodony (Hungary)

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Design/Layout

Layout	www.krea.tif–design.de
Print	www.kerndruck.de
Circulation	400
Editorial Deadline	18 August 2014

Welcome Note by the Conference Chairs

Dear MECC2014 participants, honoured guests and sponsors!

On behalf of the organizing team it is our pleasure to welcome you to the 7th Mid-European Clay Conference held in Dresden. This conference is the first one organized by the DTTG, the German Clay and Clay Minerals Group, who joined the MECC-organizing countries in 2008. With Dresden, near Meissen, we have chosen a venue with significant historic meaning for the usage of kaolinite-rich clays.

Excursions to still operating, but ancient clay pits will augment our scientific programme, which encompasses eleven sessions dealing with a multitude of currently relevant aspects of clay science. Five plenary talks and six keynotes will structure each conference day, where more than 230 participants will learn about 90 posters and 130 talks.

Our sincere thanks go to all our colleagues, who spent timeless hours with reviewing abstracts and organizing and chairing the sessions, to the team of Conventus, who took over the financial and administrative tasks and, last but not least, to our sponsors, ensuring the financial success of the conference.

We wish you an enjoyable conference with plenty of interesting presentations, fruitful discussions, reunion with colleagues and meeting our scientific future, the young students.
See you in Dresden.

Helge Stanjek
Chair, 7th MECC 2014

General Information

Venue

Radisson Blu Park Hotel
Nizzastraße 55
01445 Radebeul, nearby Dresden (DE)

Date

16–19 September 2014

Registration

Registration for the conference is required. Please register online at www.mecc2014.de. Registration can also be made via fax or mail.

Registration Fees

Regular*	470 EUR
Students*/**	280 EUR
Accompanying Person	70 EUR
Welcome Party, 16 September 2014	0 EUR
Social Evening, 18 September 2014	60 EUR
Sightseeing tour Dresden by bus 1 (18 September 2014, 15^{10}–17^{10} hrs) – Registration required.	0 EUR
Sightseeing tour Dresden by bus 2 (18 September 2014, 17^{10}–19^{10} hrs) – Registration required.	0 EUR
Field trips	
Field trip 1 Clays and Clay Deposits in Bavaria	
Overnight stay in a double room	300 EUR
Overnight stay in a single room	330 EUR
Field trip 2 Kaolin- and Clay Deposits and Mining in the Meissen Area	55 EUR
Field trip 3 Mining and Processing of Clays and Kaolins in Eastern Saxony	55 EUR
Field trip 4 Freiberg – Minerals and Mining	75 EUR

* Members of MECC Clay Groups receive 20 EUR discount

** Please send a confirmation of your status either to registration@conventus.de, Fax +49 3641 31 16-244 or by mail to Conventus GmbH • indicating the keyword: MECC2014 • Carl-Pulfrich-Straße 1 • 07745 Jena, Germany

Payment and Confirmation of Payment

An invoice or confirmation of registration will be sent to you via postal or electronic mail within 14 days. This invoice is a valid invoice which may be submitted to the local tax and revenue office. All fees are due upon receipt of invoice/registration confirmation. Payment transfers must include participant's name and invoice number. Payment is also accepted by credit card (Master-/Eurocard, American Express, VISA). Should you transfer your invoice amount within 10 days of the start of the event, please present your transfer remittance slip onsite.

The registration fees include
- Admission to all scientific sessions and access to our industrial exhibition
- Welcome reception
- Conference materials (conference bag, final programme with abstract publication, name badge, (etc.)
- Food and beverages during the breaks free of charge

Accommodation

Room allotment is reserved in the Radisson Blu Park Hotel, Nizzastraße 55, 01445 Radebeul, Germany. Please quote the special conference booking code "MECC2014" and use the booking form (download at the conference website), to benefit from the special conference rates until 18 August 2014.

Conventus acts as an intermediary for hotel reservations and therefore assumes no liability for reservations. Changes and cancellations have to be addressed to the hotel directly. The cancellation terms of the hotel apply.

General Terms and Conditions

Please find our General Terms and Conditions at www.mecc2014.de.

General Information

Travel

Arriving by train

DB German Rail Event Ticket

In cooperation with DB German Rail and Conventus you travel safely and conveniently to the 7th Mid-European Clay Conference.

The price for your event ticket of a return trip* to Dresden is:

2nd class	99 EUR (for a defined train connection)
1st class	159 EUR (for a defined train connection)

2nd class	139 EUR (for all trains)
1st class	199 EUR (for all trains)

* An advance booking of at least three days is required. Changes and reimbursement before the first day of validity are Euro 15 excluded from the first day of validity onwards. Passengers restrict themselves to a particular train and travel times. For a supplement of Euro 40 full flexible tickets are also available for domestic travels within Germany.

Please find more detailed information on conditions and booking at www.mecc2014.de.

From central station Dresden:

- from Dresden central station take S-Bahn 1 direction 'Meissen' to 'Radebeul Ost'
- Walking distance 900 m. Please follow the signage.

Arriving by car

The Radisson Blu Park Hotel & Conference Centre is just a few minutes walk from the centre of Radebeul. It is only 7 km to the historic centre of Dresden.

Venue (for navigation devices)
Radisson Blu Park Hotel
Nizzastraße 55
01445 Radebeul (DE)

Arrival by plane

Distance from airport to the Radisson Blu Park Hotel and Conference Centre: 10 km

By public transportation (nearly 45 minutes):

- from Dresden airport with S-Bahn 2 direction ‘Heidenau’ to the station ‘Dresden•Neustadt’
- 9 minutes/350 m walk: turn right in front of the station (direction south) along ‘Antonstraße’ until tram station ‘Antonstraße’
- Continue with tram 4 direction ‘Radebeul•West’ or ‘Weinboehla’ until stop ‘Schildenstraße’

OR

- from Dresden airport with bus 80 direction ‘Omsewitz’ to the station ‘Rankestraße’
- from Dresden ‘Rankestraße’ with tram 4 direction ‘Radebeul•West’ or ‘Weinboehla’ until stop ‘Schildenstraße’
  Costs: 3,90 EUR

By taxi:

With a taxi you can drive from the airport to the hotel within 10 minutes.
Taxis are available in front of the airport.
Costs: 21–25 EUR

Opening Hours	Tuesday	Wednesday	Thursday	Friday
Industrial exhibition	19^{00}–20^{00} hrs	09^{30}–19^{00} hrs	09^{30}–15^{40} hrs	09^{30}–16^{30} hrs
Check-In	17^{00}–20^{00} hrs	07^{30}–20^{30} hrs	07^{30}–18^{30} hrs	07^{30}–18^{40} hrs
Media Check In		07^{30}–20^{30} hrs	08^{00}–17^{00} hrs	08^{00}–16^{30} hrs

Internet

WIFI is available free of charge throughout the whole hotel area. You will get the login data at the check-in.

General Guidelines for Authors and Presenters

Submission of a presentation/technical information

The presentations should be prepared as PDF, MS Office PowerPoint2007, 2010 for Windows or key for Macintosh DVD in format 4:3. A presentation notebook with a PDF reader and MS Office PowerPoint 2010/2007 will be provided. The use of personal notebooks is possible upon agreement. However, it may interrupt the flow of the programme in the lecture hall. Please provide an adapter for VGA if necessary. A notebook, presenter and laser pointer are available at the speaker's podium in the lecture hall. A technical supervisor will help you. To guarantee a smooth running programme please upload your presentation on time – at least 2 hours before your presentation starts. Should you wish to use non-digital equipment, please contact us at mecc2014@conventus.de.

Presentation Upload

Please submit your presentation at the Media Check In (Tagung 7). All authors can view and/or edit their presentation in the speakers ready room. For submission, please use a USB flash drive. Professional staff and equipment will be available for you to arrange and preview your presentation.

Time Allotment

Please prepare your presentation for the allotted amount of time. Chairs and moderators may interrupt should you overrun your time limit.

Poster Session

Posters should be no larger than DIN A0 portrait format (84.1 cm x 118.9 cm). Poster boards are 120 cm x 150 cm. Pins will be provided on your poster board. All poster boards will be labeled with a poster number. You will find your poster number in the programme book on page 54 ff. Poster should be removed by Friday, 19 September 2014, 13^{30} hrs.

Sponsors

We would like to thank the following exhibitors and sponsors for their great support:

Premium Sponsors

Carl Zeiss Microscopy GmbH (Jena/DE)

NETZSCH-Gerätebau GmbH (Selb/DE)

Sponsor Lanyards

PANalytical GmbH (Kassel/DE)

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Sponsors

Analytik Jena AG (Jena/DE) (Oral presentation in the scientific programme)
Carl Zeiss Microscopy GmbH (Jena/DE) (Oral presentation in the scientific programme)
Clay Minerals Group (Twickenham/GB)
Retsch Technology GmbH (Haan/DE)
Röntgenlabor Dr. Ermrich (Reinheim/DE)
Schweizerbart/Borntraeger Science Publishers (Stuttgart/DE)
TU Bergakademie Freiberg (Freiberg/DE)

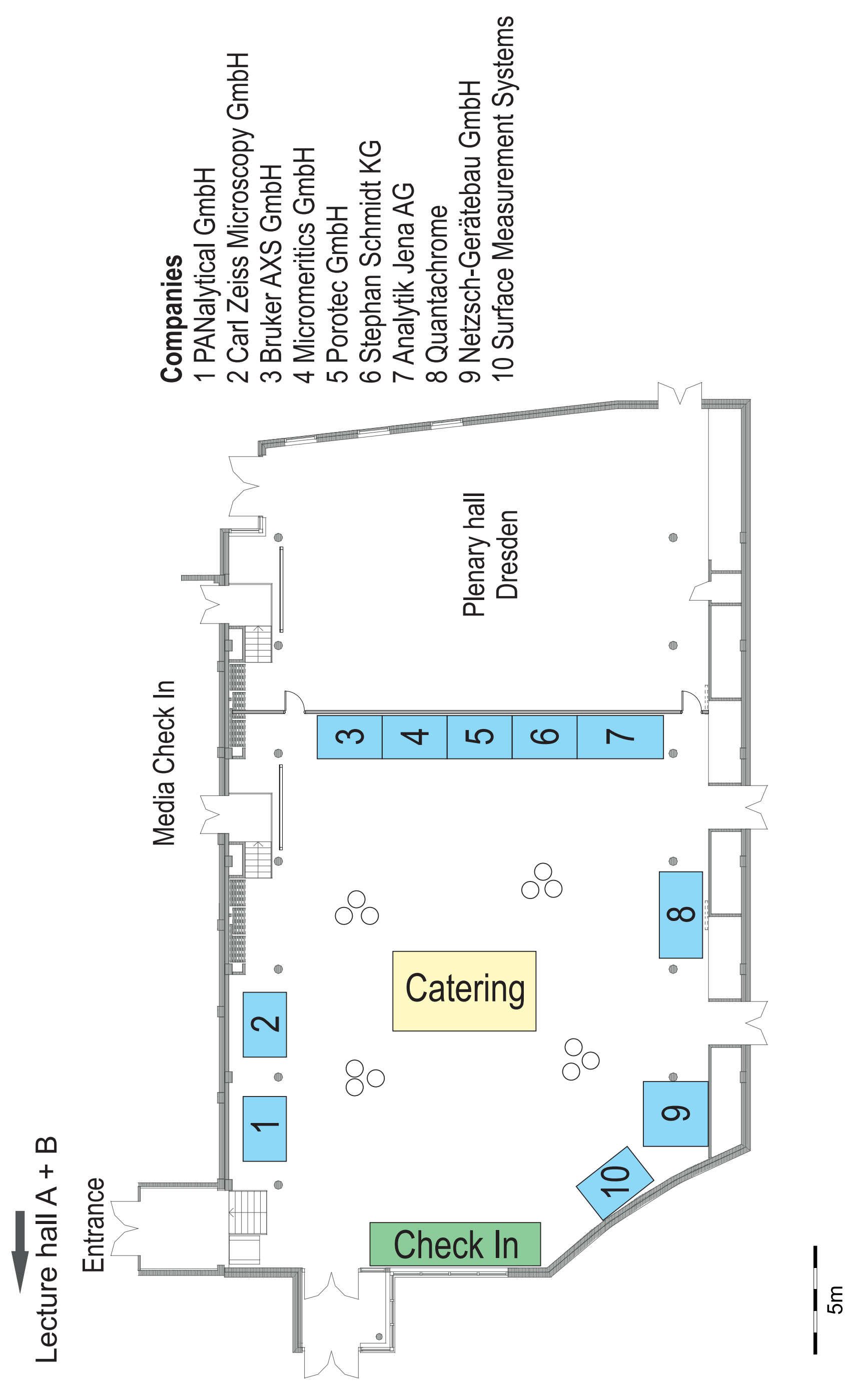
Especially, we would like to thank the Deutsche Forschungsgemeinschaft (DFG) for their great support.

Exhibitors

The following exhibitors are looking forward to greeting you and to present you their comprehensive range of innovative products:
Analytik Jena AG (Jena/DE)
Bruker AXS GmbH (Karlsruhe/DE)
Carl Zeiss Microscopy GmbH (Jena/DE)
Micromeritics GmbH (Aachen/DE)
NETZSCH-Gerätebau GmbH (Selb/DE)
PANalytical GmbH (Kassel/DE)
Porotec GmbH (Hofheim Ts./DE)
Quantachrome (Odelzhausen/DE)
Stephan Schmidt KG (Dornburg/DE)
Surface Measurement Systems (London/GB)

State at Printing

Floor Plan



Companies
1 PANalytical GmbH
2 Carl Zeiss Microscopy GmbH
3 Bruker AXS GmbH
4 Micromeritics GmbH
5 Porotec GmbH
6 Stephan Schmidt KG
7 Analytik Jena AG
8 Quantachrome
9 Netzsch-Gerätebau GmbH
10 Surface Measurement Systems

Welcome Reception

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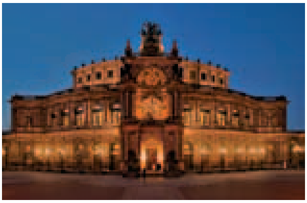
Come together for drinks and snacks to start the conference together and enjoy the first evening. Allow yourself interesting conversations with colleagues, old friends, exhibitors and meet new acquaintances.

Tuesday, 16 September 2014

Time	19^{00}–20^{00} hrs
Venue	Industrial Exhibition

Sightseeing Tours Dresden



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Don’t miss the chance to participate in an entertaining and interesting sightseeing tour with a double-decker bus. The tour will lead you through the historical center of Dresden, along the beautiful ‘Elbauen’, to the castles along the river Elbe and to lots of other famous places. During the tour a guide will tell you all the worth-knowing facts about the city.

Sightseeing Tour 1	**Sightseeing Tour 2**
Thursday, 18 September 2014	Thursday, 18 September 2014
Time: 15^{10}–17^{10} hrs	Time: 17^{10}–19^{10} hrs
Language: English	Language: English
Meeting point: main entrance	Meeting point: main entrance
End: Radisson Blu Parkhotel	**End: Historischer Güterboden (Social Evening)**
max. 80 participants	max. 80 participants

The bus tours are free of charge but a registration is required.

Social Evening at Historischer Güterboden

© www.eventlokation.de

The event location ‘Historischer Güterboden’ is a historic railway building where tradition and innovation is combined in a harmonic way. In the past, the ‘Historischer Güterboden’ was a transfer site for lots of goods of the light railway. Today it is rebuilt to a modern event location that also includes a museum with historic and listed trains. It offers an impressive original atmosphere and gives our dinner a perfect ambience.Enjoy this unique atmosphere after a long conference day!

Thursday, 18 September 2014

Time	19^{15}–24^{00} hrs
Fee	60 EUR

Address: Historischer Güterboden Radebeul • Am Alten Güterboden 4 • 01445 Radebeul Ost

Distance to the conference venue	ca. 1 km

Field Trips

1 Clays and Clay Deposits in Bavaria (Transfer Munich-Dresden-Munich)

H. Albert Gilg

3 Day Transfer Excursion Munich-Dresden-Munich (**15/16 and 20 September 2014**)
Start: 15 September 2014 – Munich City (TUM near Central Station) 08^{00} hrs and airport 09^{00} hrs
Overnight in Regensburg. Arrival in Dresden on 16 September at 17^{00} hrs.
After the MECC, a return trip to Munich Saturday 20 September. Arrival at the airport at 18^{00} hrs.

Fee
Overnight stay in a double room: 300 EUR
Overnight stay in a single room 330 EUR
Overnight stay in a double room will be with another participant.
min. 6 participants, max. 14 participants (with limited space for luggage)

Included in the fee are the transfer Munich-Radebeul-Munich, hotel with breakfast in Regensburg, lunch packets, beverages and an excursion guide. Appropriate shoes (boots) are required.

Highlights

- Landshut bentonite deposits
  (world-class Miocene bentonites derived from distal rhyolitic ashes in a terrestrial fluvial to lacustrine environment with pedogenic microbial dolomites and calcites)
- Ponholz refractory clay and lignite deposit
  (Miocene sedimentary kaolinitic clays with siderite concretions, lignite beds with fossil trees and a tonstein horizon)
- Glauconites (Regensburg Formation)
  (Upper Cretaceous marine sandstones and black shales with a spectacular discordance on a Carboniferous porphyritic granite)
- Hirschau-Schnaittenbach kaolin, feldspar and quartz deposit
  (largest kaolin deposit in Germany, Lower Triassic arkose altered to kaolinite with locally abundant crandallite group minerals)
- Neuburg siliceous earth deposit
  (Karst-hosted Upper Cretaceous marine sediments rich in nano-sized silica)
- Clay minerals in suevites of the Ries impact crater
  (Impact-induced hydrothermal versus supergene clays in the Miocene surficial melt-rich breccia deposits)

2 Kaolin- and Clay Deposits and Mining in the Meissen Area

Reinhard Kleeberg • Jan-Michael Lange

Programme: Volcanic rocks of the Meissen massif (“Pitchstone”), alteration and weathering (zeolites, smectite, ordered illit/smectite, kaolinite), kaolin- and clay deposits Seilitz and Löthain-Mehren (SIBELCO Deutschland GmbH), museum of underground clay mining “Glückauf-Schacht” Mehren, Bus trip (approx. 70 km)

Tuesday, 16 September 2014

Time	ca. 08^{00}–18^{00} hrs
Fee	55 EUR

min. 15 participants, max. 25 participants

Included in the fee is the bustour, lunch, beverages and an additional lunchbox.

3 Mining and Processing of Clays and Kaolins in Eastern Saxony

Ralf Diedel • Katrin Kleeberg

Preliminary programme: Refractory clays Wetro (P-D Refractories GmbH), filler kaolin production Caminau (Quarzwerke Gruppe)

Tuesday, 16 September 2014

Time	ca. 08^{00}–18^{00} hrs
Fee	55 EUR

min. 15 participants, max. 17 participants

Included in the fee is the bustour, beverages and a lunchbox.

4 Freiberg - Minerals and Mining

Andreas Massanek

Programme: Freiberg Mineral collections “Terra Mineralia” and the “Krügerhaus”, mineralogical institute, historical silver-lead-zinc mine “Reiche Zeche”/”Alte Elisabeth” with underground trip. Please note: The underground trip is not possible for handicapped people.

Tuesday, 16 September 2014

Time	ca. 08^{00}–18^{00} hrs
Fee	75 EUR

min. 15 participants, max. 25 participants

Included in the fee is the bustour, entrance fees, lunch at the Beachclub 7, beverages and an additional lunchbox.

Overview Plenary and Keynote Speakers

Plenary Speakers

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Institute of Inorganic Chemistry
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ANT – Analytical tools for improved characterization of clays and clay minerals
Katja Emmerich, Arkadiusz Derkowski, Georgios Chryssikos

CRY – Crystal structure of clay minerals
Kristian Ufer, Eric Ferrage

GS – General session
Jan Srodon, Reinhard Kleeberg

GTA – Clays in geotechnical applications
Michael Plötze, Tom Schanz

HYD – Clay minerals in hydro- and geothermal systems
Albert Gilg, Michal Skiba

IND – Industrial clays
Stephan Kaufhold, Ralf Diedel

PAI – Properties and processes at the aqueous interface of clay minerals
Thorsten Schäfer, Helge Stanjek

RRE – Clays, reservoir rocks and energy issues
Pieter Bertier, Andreas Busch, Reinhard Gaupp, Georg Grathoff

RWD – Stability of engineered clay barriers in radioactive waste disposal
Reiner Dohrmann, Patrik Sellin

SYS – Clays and clay-sized minerals in soils and young sediments
Karin Eusterhues, Goran Durn, Robert Mikutta

VLG – Clay minerals in diagenetic and low temperature metamorphic environments
Rafael Ferreiro Mählmann, Laurence Warr

Announcement 6th DTTG workshop

Qualitative and quantitative analysis of clays and clay minerals

9th to 13th March 2015 at Karlsruhe Institute of Technology,
Campus North

Overview lectures, laboratory exercises and computer tutorials will be combined in this 5 day workshop. The content focuses on the needs of graduate students and PhD students in the field of clay science and is also open for scientists and people working in industry who are interested in clay science. The number of participants is limited to 15.

Topics

Clays and Clay minerals
Mixed layer minerals
Diagnostic Intercalation
Qualitative and quantitative X-ray diffraction analysis, Rietveld analysis
Simultaneous thermal analysis
Fourier-transform infrared spectroscopy
Electron microscopy
Cation exchange capacity and layer charge measurements
Surfaces
Water binding
Sorption processes

Registration fees

Students	300 EUR
Scientists (University or Governmental Organizations)	600 EUR
Industry	1,100 EUR

The fees include workshop material, coffee breaks and workshop dinner.

For further information: www.dttg.ethz.ch/workshop2015.html

Programme Overview • Tuesday, 16 September 2014

Tuesday, 16 September 2014			
09:00–18:00	08:00–18:00	08:00–18:00	08:00–18:00
Fiels trip 1 Transfer from Munich Clays and Clay Seposits in Bavaria p. 14	Fiels trip 2 Kaolin- and Clay Deposits and Mining in the Meissen Area p. 15	Field trip 3 Mining and Processing of Clays and Kaolins in Eastern Saxony p. 15	Field trip 4 Freiberg - Minerals and Mining p. 15
19:00–20:00			
Welcome Reception p. 13			

🟦 Field trips

🟧 Social Programme

The industrial exhibition will be open from 19:00-20:00.

Programme Overview • Wednesday, 17 September 2014

Wednesday, 17 September 2014			
Lecture hall "Dresden"	Lecture hall A	Lecture hall B	Foyer
08:30–08:50 Opening p. 23			
08:50–09:30 Plenary Lecture Fernando Nieto Garcia p. 23			
09:50–11:20 Clay minerals in diagenetic and low temperature metamorphic environments I p. 23	09:50–11:20 Properties and processes at the aqueous interface of clay minerals I p. 24	09:50–11:20 Crystal structure of clay minerals I p. 25	
11:50–13:30 Clay minerals in diagenetic and low temperature metamorphic environments II p. 26	11:50–13:30 Properties and processes at the aqueous interface of clay minerals II p. 27	11:50–13:30 Crystal structure of clay minerals II p. 28	
14:20–15:00 Plenary Lecture Boris Sakharov p. 29			
15:20–17:00 Clay minerals in diagenetic and low temperature metamorphic environments III p. 29	15:20–17:00 Properties and processes at the aqueous interface of clay minerals III p. 30	15:20–17:00 Industrial clays I p. 31	
17:30–18:50 General session I p. 32	17:30–18:30 Crystal structure of clay minerals III p. 33	17:30–18:50 Industrial clays II p. 34	
	19:00–20:00 MECC Meeting p. 34		19:00–20:00 Poster Session I p. 54

🟧	Social Programme	🟩	Plenary Lectures
🟦	Oral Abstract Sessions	🟦	Poster Session
🟪	Meetings	🟥	Opening

The industrial exhibition will be open from 09:30-19:00. Food and beverages will be served during the coffee and lunch breaks.

Programme Overview • Thursday, 18 September 2014

Thursday, 18 September 2014				
Lecture hall "Dresden"	Lecture hall A	Lecture hall B	Foyer	
08:30–09:20 The Lagaly Award Lecture Juraj Bujdak p. 35				
09:40–11:10 Stability of engineered clay barriers in radioactive waste disposal I p. 35	09:40–11:10 Clays and clay-sized minerals in soils and young sediments I p. 36	09:40–11:10 Clays, reservoir rocks and energy issues I p. 37		
11:40–13:20 Stability of engineered clay barriers in radioactive waste disposal II p. 38	11:40–13:20 Clays and clay-sized minerals in soils and young sediments II p. 39	11:40–13:20 Clays, reservoir rocks and energy issues II p. 40		
14:20–15:00 Plenary Lecture Steve Hillier p. 41				
	15:20–16:40 ECGA Meeting p. 41		15:20–16:40 Poster Session II p. 54	15:10–17:10 Sightseeing tour Dresden by bus I p. 13
17:00–18:00 DTTG Meeting p. 41	17:00–18:00 Round table to discuss problems in "Kübler Index" standardisation p. 41			17:10–19:10 Sightseeing tour Dresden by bus II p. 13
19:00–24:00 Social Evening at the 'Historischer Güterboden' p. 13				

🟧	Social Programme	🟩	Plenary Lectures
🟦	Oral Abstract Sessions	🟦	Poster Session
🟪	Meetings		

The industrial exhibition will be open from 09:30-15:40. Food and beverages will be served during the coffee and lunch breaks.

Programme Overview • Friday, 19 September 2014

Friday, 19 September 2014		
Lecture hall "Dresden"	Lecture hall A	Lecture hall B
08:30–09:20		
The Clay Minerals Group Lecture Mark Wilkinson p. 42		
09:40–11:20	09:40–11:20	09:40–11:20
Industrial clays III p. 42	Clays in geotechnical applications I p. 43	Analytical tools for improved characterization of clays and clay minerals I p. 44
11:50–13:30	11:50–13:30	11:50–13:30
General session II p. 45	Clays in geotechnical applications II p. 46	Analytical tools for improved characterization of clays and clay minerals II p. 47
14:20–15:20	14:20–15:40	14:20–16:00
Clays in geotechnical applications III p. 48	Clays, reservoir rocks and energy issues III p. 49	Analytical tools for improved characterization of clays and clay minerals III p. 50
15:20–16:00		
Clay minerals in hydro- and geothermal systems I p. 48		
16:20–17:40	16:20–17:40	16:20–17:40
Clay minerals in hydro- and geothermal systems II p. 51	Clays, reservoir rocks and energy issues III p. 52	Clays and clay-sized minerals in soils and young sediments III p. 53
17:50–18:30		
Closing including Students awards p. 53		

🟩	Plenary Lectures
🟦	Oral Abstract Sessions
🟥	Closing

The industrial exhibition will be open from 09:30-16:30. Food and beverages will be served during the coffee and lunch breaks.

Lecture hall Dresden

08^{30}–08^{50} Opening

08^{50}–09^{30} Plenary Session
Chair Rafael Ferreiro Mählmann (Darmstadt/DE)

P01 **The physical meaning of clay mineral indices and reaction progress in pelitic rocks**
Fernando Nieto García (Granada/ES)

09^{50}–11^{20} Clay minerals in diagenetic and low temperature metamorphic environments I
Chair Fernando Nieto García (Granada/ES)

09^{50} Keynote lecture: **Illite+smectite as components of shales**
VLG-T01 Jan Srodoń (Krakow/PL)

10^{20} **20 years of the Crystallinity Index Standard – a progress report**
VLG-T02 Laurence Warr (Greifswald/DE)

10^{40} **Standardisation, calibration and correlation of the Kübler-Index**
VLG-T03 Rafael Ferreiro Mählmann, Thanh Lan Nguyen (Darmstadt/DE)

11^{00} **Low-grade metamorphic study based on Árkai Index and Kübler Index correlation in basins of Southern Vosges (NE France)**
VLG-T04 Sébastien Potel, Delphine Chassagnac, Mathilde Laffay, Marine Maillet, Anta-Clarisse Sarr, Michael Doublier (Beauvais/FR)
Rafael Ferreiro Mählmann (Darmstadt/DE)

Lecture hall B

09^{50}–11^{20} Properties and processes at the aqueous interface of clay minerals I

Chair Thorsten Schäfer (Karlsruhe/DE)

09^{50} Keynote Lecture: **Water at interfaces – the potential effect of water structure on charging phenomena**
PAI-T01 Johannes Lützenkirchen (Karlsruhe/DE)

10^{20} **Cation diffusion in the interlayer space of swelling clay minerals – a combined macroscopic and microscopic study**
PAI-T02 Emmanuel Tertre (Poitiers/FR), Alfred Delville (Orléans/FR), Dimitri Prêt
Fabien Hubert, Eric Ferrage (Poitiers/FR)

10^{40} **Ion exchange of major inorganic cations (Na, K, Ca, Mg, H) on beidellite: Experimental and modeling approach**
PAI-T03 Valentin Robin, Emmanuel Tertre, Daniel Beaufort, Paul Sardini (Poitiers/FR)
Olivier Regnault, Michael Descostes (Paris La Défense/FR)

11^{00} **Cs+-for-Na+ exchange on vermiculite – influence of particle size**
PAI-T04 Liva Dzene, Emmanuel Tertre, Fabien Hubert, Eric Ferrage (Poitiers/FR)

Lecture hall A

09^{50}–11^{20} Crystal structure of clay minerals I
Chair Kristian Ufer (Hannover/DE)

09^{50} Keynote Lecture: **The phyllomanganates – crystal structure of a large family**
CRY-T01 Anne-Claire Gaillot (Nantes/FR), Victor Drits (Moscow/RU), Alain Manceau
Martine Lanson, Bruno Lanson (Grenoble/FR)

10^{20} **Structure of nanocrystalline calcium silicate hydrates**
CRY-T02 Sylvain Grangeon, Francis Claret, Catherine Lerouge (Orléans/FR)
Bruno Lanson (Grenoble/FR)

10^{40} **Structure of phyllosilicates as a challenge for functional nanostructures**
CRY-T03 Pavla Capková (Usti nad Labem/CZ), Jonáš Tokarský, Lenka Kulhánková
Vlastimil Matějk, Pavlina Peikertová, Lucie Neuwirthová
Vítězslav Stýskala (Ostrava/CZ)

11^{00} **Comparison of different force fields by coupling molecular simulations of**
CRY-T04 **organo-clayswith X-ray diffraction data**
Marek Szczerba (Kraków/PL), Andrey G. Kalinichev (Nantes/FR)

Lecture hall Dresden

11^{50}–13^{30} Clay minerals in diagenetic and low temperature metamorphic environments II

Chair Laurence Warr (Greifswald/DE)

11^{50}
VLG-T05 **Differences of maturation between clays and organic matter in materials altered by the Monchique pluton (South Portugal)**
Fernando Nieto (Granada/ES), Isabel Abad (Jaén/ES), Nicolás Velilla (Granada/ES)
Isabel Suárez-Ruiz (Oviedo/ES)

12^{10}
VLG-T06 **Diagenesis and metamorphism of the Meso-Neoproterozoic and the Lower Paleozoic along profile Yueyang-Linxiang in northeastern Hunan province, China**
Hejing Wang, Lei Yuan, Ling Wang, Zhao Zhou (Beijing/CN)

12^{30}
VLG-T07 **New insights in the definition of phyllosilicate stacks in diagenetic-metamorphic environments – examples from clastic to metaclastic rocks in Turkey**
Ömer Bozkaya (Denizli/TR), Hüseyin Yalçın (Sivas/TR), Paul A. Schroeder
Doug Crowe (Athens, GA/US)

12^{50}
VLG-T08 **Chlorite crystallizations induced by fluid circulation and deformation along a thrust fault zone (Pic de port vieux thrust, Pyrenees)**
Vincent Trincal, Martine Buatier, Delphine Charpentier (Besançon/FR)
Pierre Lanari (Bern/CH), Brice Lacroix (Ann Arbor, MI/US)
Pierre Labaume (Montpellier/FR), Manuel Muñoz (Grenoble/FR)
Abdeltif Lahfid (Orléans/FR)

13^{10}
VLG-T09 **Dewatering path-ways evidenced by clay minerals in a diagenetic/very low-grade tectono-metamorphic mélange (Arosa zone, CH)**
Rafael Ferreiro Mählmann (Darmstadt/DE)

Lecture hall B

11^{50}–13^{30} Properties and processes at the aqueous interface of clay minerals II

Chair Helge Stanjek (Aachen/DE)

11^{50} **The interaction between bentonite and water vapor**
PAI-T05 Michel Heuser, Christian Weber, Helge Stanjek (Aachen/DE)
Hong Chen (Mol/BE), Guntram Jordan, Wolfgang Schmahl (Munich/DE)
Carsten Natzeck (Karlsruhe/DE)

12^{10} **Preparation and characterization of kaolinite nanostructures**
PAI-T06 Balázs Zsirka, Erzsébet Horváth, János Kristóf, Éva Makó
András Dallos (Veszprém/HU)

12^{30} **Influence of particle size and mineralogy on edge sites reactivity of montmorillonite**
PAI-T07 Laure Delavernhe, Annett Steudel, Gopala Krishna Darbha, Thorsten Schäfer
Rainer Schuhmann, Christof Wöll, Horst Geckeis
Katja Emmerich (Karlsruhe/DE)

12^{50} **Acid leaching of Fe-riched clays – effect on adsorption properties**
PAI-T08 Barbora Dousova, David Kolousek, Miloslav Lhotka, Petra Spurna
Petra Houdkova, Lenka Holcova (Prague/CZ)

13^{10} **Preparation and photochemical application of kaolinite-silver nanocomposites**
PAI-T09 János Kristóf, Erzsébet Horváth, Balázs Zsirka, Éva Makó (Veszprém/HU)

Lecture hall A

11^{50}–13^{30} Crystal structure of clay minerals II
Chair Eric Ferrage (Poitiers/FR)

11^{50} **Modelling the diffraction pattern of lamellar materials – structure, microstructure, and faulting**
CRY-T05 Robert Koch, Matteo Leoni (Trento/IT)

12^{10} **Identification and quantification of complex soil clay mineralogy by using X-ray diffraction profile modelling**
CRY-T06 Fabien Hubert, Jean Christophe Viennet (Poitiers/FR), Bruno Lanson (Grenoble/FR) Emmanuel Tertre, Eric Ferrage (Poitiers/FR)

12^{30} **Aluminoceladonites – crystal-chemical peculiarities, identification and occurrence**
CRY-T07 Bella Zviagina, Victor Drits (Moscow/RU)

12^{50} **High temperature studies on zinnwaldite – structural changes up to 800°C**
CRY-T08 Anke Hertam, Wolfgang Voigt (Freiberg/DE)

13^{10} **Characterization of iron sites in a fine grained illite**
CRY-T09 Frank Friedrich (Karlsruhe/DE), Christian Bender-Koch (Copenhagen/DK)

Lecture hall Dresden

14^{20}–15^{00} Plenary Session

Chair Eric Ferrage (Poitiers/FR)

P02 **Simulation of XRD patterns of clay mineral defective structures**
Boris Sakharov (Moscow/RU)

15^{20}–17^{00} Clay minerals in diagenetic and low temperature metamorphic environments III

Chair Rafael Ferreiro Mählmann (Darmstadt/DE)

15^{20}
VLG-T10 **Illitization of Ordovician bentonites in Baltic Basin – Where all this K was taken from?**
Peeter Somelar, Kalle Kirsimäe (Tartu/EE)

15^{40}
VLG-T11 **The role of deep-water glauconitization in the sedimentary iron cycle**
Andre Baldermann (Graz/AT), Laurence Warr (Greifswald/DE), Ilse Letofsky-Papst
Vasileios Mavromatis (Graz/AT), Michael Böttcher (Warnemünde/DE)

16^{00}
VLG-T12 **Controlling factors of alteration rate of basaltic glass and palagonite formation in pillow lavas from Hawaii Scientific Drilling Project**
Stefan Dultz, Harald Behrens, Christoph Dupont, Fabian Tramm
Christoph Ohrt (Hannover/DE), Michael Plötze (Zurich/CH)

16^{20}
VLG-T13 **Petrography and crystal-chemistry of authigenic beidellite in the Eocene sandy sediments of the Chu-Saryssu basin (Kazakhstan)**
Valentin Robin, Benoit Hebert (Poitiers, Paris La Défense/FR), Daniel Beaufort
Paul Sardini, Emmanuel Tertre (Poitiers/FR), Olivier Regnault
Michael Descostes (Paris La Défense/FR)

16^{40}
VLG-T14 **Weathering, sedimentary, and diagenetic controls of mineral and geochemical characteristics of the vertebrate-bearing Silesian Keuper**
Jan Srodoń, Joachim Szulc, Aneta Anczkiewicz (Krakow/PL)
Karol Jewuła (Krakow/PL; Welshpool/GB), Michał Banaś (Krakow/PL)
Leszek Marynowski (Krakow, Sosnowiec/PL)

Lecture hall B

15^{20}–16^{40} Properties and processes at the aqueous interface of clay minerals III
Chair Emmanuel Tertre (Poitiers/FR)

15^{20} **Sorption and desorption of soluble organic matter in Boom Clay**
PAI-T10 Delphine Durce, Christophe Bruggeman, Norbert Maes (Mol/BE)

15^{40} **Sorption efficiency of selected metals on kaolinites grafted with aminoalcohols**
PAI-T11 Anna Koteja, Jakub Matusik (Krakow/PL)

16^{00} **Adsorption of tiabendazole on organically modified montmorillonite**
PAI-T12 Petr Kovář (Prague /CZ), Martina Gamba, R. M. Torres Sánchez (Buenos Aires/AR)

16^{20} **Adsorption of Indigo carmine from aqueous solution onto montmorillonite**
PAI-T13 **using full factorial design**
Feza Geyikçi (Samsun/TR)

Lecture hall A

15^{20}–17^{00} Industrial clays I

Chair Stephan Kaufhold (Hannover/DE)

15^{20} **Identification of sodium carbonate activated bentonites**
IND-T01 Stephan Kaufhold (Hannover/DE), Katja Emmerich (Karlsruhe/DE)
Reiner Dohrmann (Hannover/DE), Annett Steudel (Karlsruhe/DE)
Kristian Ufer (Hannover/DE)

15^{40} **Characterization of the bulk and microrheological properties of arrested states**
IND-T02 **in dilute natural clay mineral dispersions**
Müge Pilavtepe, Norbert Willenbacher, Annett Steudel, Rainer Schuhmann
Katja Emmerich (Karlsruhe/DE)

16^{00} **Improved quality control of basaltic crushed stone**
IND-T03 Stephan Kaufhold, R. Dohrmann, H. G. Dill (Hannover/DE)

16^{20} **Effect of two organophilic modifiers on properties of organoclay-polymer**
IND-T04 **nanocomposites**
Ľuboš Jankovič, Daniela Jochec-Mošková, Jana Madejová
Ivan Chodák, Peter Komadel (Bratislava/SK)

16^{40} **Metronidazole/Montmorillonite nanodevices for controlled drug delivery**
IND-T05 Ilaria Calabrese, Luciana Sciascia, Gennara Cavallaro, Cinzia Scialabba
Mariano Licciardi, Marcello Merli, Maria Liria Turco Liveri (Palermo/IT)

Lecture hall Dresden

17^{30}–18^{50} General Session I

Chair Jan Srodon (Krakow/PL)

17^{30}
GS-T01 **Geochemical study of dolomite and smectite from non-marine bentonites (Bavaria, Germany)**
Mathias H. Köster (Munich/DE), Stefan Hölzl (Nördlingen/DE)
H. Albert Gilg (Munich/DE)

17^{50}
GS-T02 **Genetical signatures of nickel-chrome-bearing nontronite and montmorillonite in lateritised ultramafic rocks in the Muratdaği region (Uşak, Western Anatolia), Turkey**
Selahattin Kadir (Eskisehir/TR), M. Selman Aydogan (Balikesir/TR)
Omer Elitok (Isparta/TR), Cahit Helvaci (Izmir/TR)

18^{10}
GS-T03 **Clay minerals in hemipelagic marl-limestone deposits – example of the latest Early Jurassic of the Lusitanian Basin (Portugal)**
Ana Caniço, Luis Vitor Duarte, Fernando Rocha (Coimbra/PT)

18^{30}
GS-T04 **Alteration of structural and physicochemical properties of clays under a 100 km overburden stress**
Martin Valter, Peter Ulmer, Michael Plötze (Zurich/CH)

Lecture hall B

17^{30}–18^{30} Crystal structure of clay minerals III

Chair Kristian Ufer (Hannover/DE)

17^{30}
CRY-T10 **Crystal-chemical controls on smectite hydration**
Baptiste Dazas, Bruno Lanson (Grenoble/FR), Eric Ferrage (Poitiers/FR)
Alfred Delville (Orléans/FR)

17^{50}
CRY-T11 **Identification of the external surfaces structure of organo-clays an XPS and MD study**
Birgit Schampera, Robert Mikutta, Susanne K. Woche (Hannover/DE)
Daniel Tunega, Roland Solc (Vienna/AT), Stefan Dultz (Hannover/DE)

18^{10}
CRY-T12 **Interlayer Li+ in dioctahedral smectites as probe for an improved structural characterization**
Annett Steudel (Karlsruhe/DE), Ralf Heinzmann (Rheinstetten/DE), Sylvio Indris
Katja Emmerich (Karlsruhe/DE)

Lecture hall A

17^{30}–18^{50} Industrial clays II

Chair Ralf Diedel (Höhr-Grenzhausen/DE)

17^{30} IND-T06 **Characterization of ceramic clays from corumbataí formation used in the Ceramic District of Santa Gertrudes (CDSG) – Brazil**
Andrezza Azzi (Rio Claro/BR), Peter Uhlík, Marek Osacký (Bratislava/SK)
Antenor Zanardo (Rio Claro/BR)

17^{50} IND-T07 **K, Ca-Na feldspar, firing schudule and mixing type effect on cristobalite formation in kaolinitic and illitic clays of Westerwald**
Ismail Aydin Aras (Van/TR)

18^{10} IND-T08 **Bentonite – a natural additive in lime-metakaolin mortars for restoration of historic buildings**
Slávka Andrejkovičová, Cátia Alves, Ana Velosa, Fernando Rocha (Aveiro/PT)

18^{30} IND-T09 **Mineralogical study of different Kaolin samples from Iran China Clay Company and possibility of ultrasound irradiation as useful treatment in future procedures**
Hamed Haghi, Mohammad Noaparast, Seyed Zia-e-din Shafaei
Mirsaleh Mirmohammadi (Tehran/IR)

Lecture hall B

19^{00}–20^{00} MECC Meeting (Delegates of the MECC National groups only)

19^{00}–20^{00} Poster Session I

Lecture hall Dresden

08^{30}–09^{20} The Lagaly Award Lecture
Chair Helge Stanjek (Aachen/DE)

08^{30} **Hybrids based on organic dyes and smectites – fundamentals and potential**
P03 **applications**
Juraj Bujdák (Bratislava/SK)

09^{40}–11^{10} Stability of engineered clay barriers in radioactive waste disposal I
Chairs Reiner Dohrmann (Hannover/DE), Patrik Sellin (Stockholm/SE)

09^{40} Keynote Lecture: **Clays and shales as long-term barriers for flow and**
RWD-T01 **contaminant transport**
Martin Mazurek (Bern/CH)

10^{10} **Role of clay minerals on the carbonate chemistry in a marine clay formation**
RWD-T02 Catherine Lerouge, Sylvain Grangeon (Orléans/FR), Martin Mazurek (Bern/CH)
Guillaume Wille (Orléans/FR)

10^{30} **Monitoring and modelling the behavior of a high pH waters injected in an**
RWD-T03 **equipped borehole of the Meuse Haute Marne Underground Research Laboratory**
Francis Claret (Orléans/FR), Yannick Linard (Centre de Meuse/Hte Marne Bure/FR)
Stephane Gaboreau (Orléans/FR), Xavier Bourbon (Châtenay-Malabry/FR)
Catherine Lerouge, Christophe Tournassat (Orléans/FR)

10^{50} **Montmorillonite as barrier material for uranium (VI) at high ionic strengths**
RWD-T04 Katharina Fritsch, Katja Schmeide (Dresden/DE)

Lecture hall B

09^{40}–11^{10} Clays and clay-sized minerals in soils and young sediments I

Chair Goran Durn (Zagreb/HR)

09^{40} Keynote Lecture: **Fe(III)-precipitates formed by Fe(II) oxidation in water:**
SYS-T01 **Structure, reactivity and impact on As**
Andreas Voegelin (Dübendorf/CH)

10^{10} **Clay mineral transformations in mangrove soils – kaolinite to Fe-illite via K-S**
SYS-T02 **and I-S mixed-layer**
Javier Cuadros (London/GB), Gabriel Andrade, Pablo Vidal (Piracicaba/BR)

10^{30} **Changes of mineral and chemical composition of soils' clay fraction result from**
SYS-T03 **microbial complex activation**
Pavel Ivanov, Viktor Trofimov, Viktoria Krupskaya, Natalia Manucharova
Sergey Zakusin (Moscow/RU)

10^{50} **The driving influence of clay minerals on establishment and functionality of soil**
SYS-T04 **microbial communities**
Doreen Babin (Braunschweig, Jena/DE)
Guo-Chun Ding (Braunschweig/DE; Beijing/CN)
Geertje Johanna Pronk (Freising-Weihenstephan, Garching/DE)
Cordula Vogel, Katja Heister (Freising-Weihenstephan/DE)
Ingrid Kögel-Knabner (Freising-Weihenstephan, Garching/DE)
Kornelia Smalla (Braunschweig/DE)

Lecture hall A

09^{40}–11^{10} Clays, reservoir rocks and energy issues I

Chairs Pieter Bertier (Aachen/DE), Andreas Busch (GS Rijswijk/NL)

09^{40} Keynote Lecture: **Clay minerals in poresystems of reservoir sandstones**
RRE-T01 Reinhard Gaupp (Jena/DE)

10^{10} **Porosity preservation in deeply buried (8552 m) mudstones of the Vienna Basin**
RRE-T02 **(Austria)**
Susanne Gier (Vienna/AT), Jürgen Schieber (Bloomington, IN/US)
Andrea Schicker (Vienna/AT)

10^{30} **Comprehensive study of clay minerals in section E of Qom formation and**
RRE-T03 **Sarajeh gas storage field**
Soheyla Aslani, Hamed Haghi, A. Dehkar, A. Bashari
Mohsen Farrokhrouz (Tehran/IR)

10^{50} **Mineralogy, chemistry and surface properties of Alberta oil sands**
RRE-T04 Marek Osacký (Bratislava/SK), Mirjavad Geramian, Douglas G. Ivey
Thomas H. Etsell, Qi Liu (Edmonton/CA)

Scientific Programme • Thursday, 18 September 2014

Lecture hall Dresden

11^{40}–13^{20} Stability of engineered clay barriers in radioactive waste disposal II

Chairs Reiner Dohrmann (Hannover/DE), Patrik Sellin (Stockholm/SE)

11^{40}
RWD-T05 **Formation of trioctahedral smectite in a 6½ year iron-bentonite large scale field experiment (ABM2) at Äspö hard rock laboratory, Sweden**
Daniel Svensson (Figeholm/SE)

12^{00}
RWD-T06 **Geochemical modelling of the ABM experiment at Äspö HRL**
Andrés Idiart, Marek Pekala, David Arcos (Barcelona/ES)

12^{20}
RWD-T07 **Kinetic experiments and XPS study of uranyl adsorption onto Ca-montmorillonite in the presence and absence of carbonates**
Vanessa Guimarães (Aveiro/PT), Iuliu Bobos (Porto/PT), Fernando Rocha (Aveiro/PT)
Manuel Algarra, Enrique Rodríguez-Castellón (Málaga/ES)

12^{40}
RWD-T08 **Laboratory and in-situ testing of gas permeability and self-healing ability of Czech Ca-Mg bentonite**
Jan Smutek, Marketa Levorova (Prague/CZ)

13^{00}
RWD-T09 **Experimental investigations of piping phenomena by saline water in bentonite based buffer materials for HLW repository**
Kei Suzuki, Hidekazu Asano, Jiro Eto, Nobumitsu Takeuchi
Ichizo Kobayashi (Tokyo/JP), Patric Sellin, Christer Svemer
Karin Pers (Stockholm/SE)

Lecture hall B

11^{40}–13^{20} Clays and clay-sized minerals in soils and young sediments II
Chair Robert Mikutta (Hannover/DE)

11^{40} **Clay minerals’ transformations in permafrost affected soils of Northern Eurasia**
SYS-T05 Sofia Lessovaia (St. Petersburg/RU)

12^{00} **Cambrian paleosol of Baltica**
SYS-T06 Ilze Vircava, Peeter Somelar, Sirle Liivamägi, Kalle Kirsimäe (Tartu/EE)

12^{20} **Investigation of hydroxy-interlayered clays in a temperate acidic soil under**
SYS-T07 **forest using X-ray diffraction profile modeling. Beyond the HIS and**
HIV description
Jean-Christophe Viennet, Fabien Hubert, Eric Ferrage
Emmanuel Tertre, Alain Meunier (Poitiers/FR)
Marie-Pierre Turpault (Nancy/FR)

12^{40} **Neoproterozoic Baltic paleosol: clay mineralogy and paleoclimatic**
SYS-T08 **interpretation**
Sirle Liivamägi, Kalle Kirsimäe, Peeter Somelar, Juho Kirs, Ilze Vircava (Tartu/EE)

13^{00} **Transformation of clay minerals in albeluvisols from the Carpathian Foothills,**
SYS-T09 **Poland**
Wojciech Szymański, Michał Skiba (Kraków/PL), Volodymyr Nikorych (Chernivtsi/UA)

Lecture hall A

11^{40}–13^{20} Clays, reservoir rocks and energy issues II

Chairs Pieter Bertier (Aachen/DE), Andreas Busch (Rijswijk/NL)

11^{40}
RRE-T05 **The swelling of smectites by high-pressure CO_2 and the possible impact on the containment of CO_2 below the caprock**
Rick Wentinck, Andreas Busch (Rijswijk/NL)

12^{00}
RRE-T06 **Water distribution in montmorillonite as a function of temperature and pressure**
Fanni Juranyi, Martina Bestel (Villigen/CH)
Johannes Breitling (Villigen/CH; Konstanz/DE), Thomas Gimmi (Villigen, Bern/CH)
Sergey V. Churakov, Luc R. Van Loon, Martin A. Glaus (Villigen/CH)
Larryn W. Diamond (Bern/CH), Michaela Zamponi (Garching/DE)

12^{20}
RRE-T07 **Swelling stress development in smectites upon exposure to CO_2 under in-situ P-T conditions**
Miao Zhang, Christopher J. Spiers (Utrecht/NL), Andreas Busch
Rick Wentinck (Rijswijk/NL)

12^{40}
RRE-T08 **Microfabric of tectonically faulted Opalinus Clay – What can it tell us about deformation mechanisms and fault properties?**
Ben Laurich, Janos L. Urai, Guillaume Desbois (Aachen/DE)
Christian Vollmer (Münster/DE), Christophe Nussbaum (Wabern/DE)

13^{00}
RRE-T09 **The cap rocks sealing the reservoir in the Węglówka Oil Field, Sub-Silesian Unit, Polish Outer Carpathians – petrographical approach**
Katarzyna Górniak (Kraków/PL)

Lecture hall Dresden

14^{20}–15^{00} Plenary Session

Chair Katja Emmerich (Karlsruhe/DE)

P04 **“Vermiculite” – What a mixture!**
Steve Hillier (Aberdeen/GB)

15^{20}–16^{40} Poster Session II

Lecture hall B

15^{20}–16^{40} ECGA Meeting (ECGA board members only)

Lecture halls

17^{00}–18^{00} Meetings of the National Clay Groups

Lecture hall B

17^{00}–18^{00} Round table to discuss problems in *Kübler Index* standardisation

19^{10}–24^{00} Social Evening at Historischer Güterboden

Scientific Programme • Friday, 19 September 2014

Lecture hall Dresden

08^{30}–09^{20} The Clay Minerals Group Lecture
Chair Steve Hillier (Aberdeen/GB)

P05 **What do experiments tell us about the rate of reaction in the real world?**
Mark Wilkinson (Edinburgh/GB)

09^{40}–11^{20} Industrial clays III
Chair Stephan Kaufhold (Hannover/DE)

09^{40}
IND-T10 **Formation of hydrotalcite coating on the Aluminum alloy in spray system**
Lingli Zhou, Henrik Friis, Melanie Roefzaad, Kasper Bondo Hansen
Nikolaj Zangenberg, Sara Eisenhardt (Aarhus/DK)

10^{00}
IND-T11 **Bentonite in papermaking – complexity of interactions in colloidal systems of real life**
Nils Rickertsen (Marl/DE)

10^{20}
IND-T12 **Innovative clay sorbents for heavy metal immobilization**
Juris Burlakovs, Zane Vincevica-Gaile, Mara Stapkevica, Maris Klavins (Riga/LV)

10^{40}
IND-T13 **Green rust and ferrihydrite–coated pozzolana as new filtration materials for water dephosphatation**
Sébastien Naille, Kévin Barthélémy (Villers-lès-Nancy/FR)
Khalil Hanna (Rennes/FR), Martine Mallet, Christian Ruby (Villers-lès-Nancy/FR)

11^{00}
IND-T14 **Use of modified montmorillonite for the oxidation of aqueous sulfide**
Mateus Castro (Belo Horizonte/BR), Mariela Fernandez (M. B. Gonnet/AR)
Rochel Lago (Belo Horizonte/BR), Rosa María Torres Sánchez (La Plata/AR)

Lecture hall B

09⁴⁰–11²⁰ Clays in geotechnical applications I

Chair Tom Schanz (Bochum/DE)

09^{40} GTA-T01 **Development of high density bimodal bentonite blends for high pressure sealings at the Ibbenbüren coal mine**
Matthias Schellhorn (Dornburg/DE), Felicitas Wolters (Dortmund/DE)
Eva Schmidt (Dornburg/DE), Jürgen Kunz (Ibbenbüren/DE)

10^{00} GTA-T02 **Permeability and swelling pressure of compacted bimodal bentonite blends for underground barriers in Ibbenbüren – Beustfeld**
Felicitas Wolters (Dortmund/DE), Volker Krase, Wiebke Baille (Bochum/DE)
Jürgen Kunz (Ibbenbüren/DE), Matthias Schellhorn (Dornburg/DE)

10^{20} GTA-T03 **SANDWICH – Multilayer hydraulic sealing system for universal underground application**
Katja Emmerich (Karlsruhe/DE), Felicitas Wolters (Dortmund/DE)
Juergen Kunz (Ibbenbüren/DE), Rainer Schuhmann (Karlsruhe/DE)

10^{40} GTA-T04 **Plasticity and water retention of bentonite-polymer composites**
Hanna Viefhaus, Tom Schanz (Bochum/DE)

Scientific Programme • Friday, 19 September 2014

Lecture hall A

09^{40}–11^{20}	Analytical tools for improved characterization of clays and clay minerals I
Chair	Arkadiusz Derkowski (Warszawa/PL)
09^{40} ANT-T01	**Quantitative mineral analysis of complex mineral assemblages – the Reynolds Cup round robins of the CMS in clay analysis** Michael Plötze (Zurich/CH)
10^{00} ANT-T02	**Identifying and fixing methodical weaknesses by participating the Reynolds Cup competition in quantitative mineral analysis** Reinhard Kleeberg, Robert Möckel, Ulf Kempe (Freiberg/DE)
10^{20} ANT-T03	**Parametric Rietveld refinement of coexisting disordered clay minerals** Kristian Ufer (Hannover/DE), Reinhard Kleeberg (Freiberg/DE)
10^{40} ANT-T04	**Characterization of synthetic trioctahedral smectites with X-ray diffraction – an attempt to evaluate smectite heterogeneity** Carlos Aldana, George Christidis (Chania/GR), Hussein Kalo (Bayreuth/DE) Eleni Koutsopoulou (Patras/GR)
11^{00} ANT-T05	**Fully automated TIC/TOC and TS analysis in clay and related matrices by multi EA® 4000** Bernd Bletzinger, Stefan Jezierski (Jena/DE)

Lecture hall Dresden

11^{50}–13^{30} General Session II
Chair Reinhard Kleeberg (Freiberg/DE)

11^{50}
GS-T05
Characterisation of clayey raw materials for Bronze Age ceramic manufacture in Turopolje (Croatia)
Marta Mileusnić, Andreja Kudelić (Zagreb/HR), Karin Wriessnig
Franz Ottner (Vienna/AT), Goran Durn (Zagreb/HR)

12^{10}
GS-T06
Smectite in ancient pottery from Hallstatt – A contradiction?
Karin Wriessnig, Verena Schiffel, Franz Ottner (Vienna/AT), Goran Durn
Marta Mileusnic (Vienna/HR)

12^{30}
GS-T07
Mineralogic-chemical and physical characteristics of the peloids in Muğla region (South-western Turkey) – suitability for use in pelotherapy
Muazzez Celik Karakaya, Necati Karakaya (Konya/TR)

12^{50}
GS-T08
Characterisation and distribution of carcinogenic amphibole and serpentine minerals and relationship with development of potential mesothelioma cases in Eskişehir, Western Turkey
Selahattin Kadir, Hülya Erkoyun (Eskişehir/TR)

13^{10}
GS-T09
Influence of synthesis method in preparation of organosmectites
Gamoudi Safa (Gafsa/TN)

Lecture hall B

11^{50}–13^{30} Clays in geotechnical applications II
Chairs Michael Plötze (Zurich/CH), Tom Schanz (Bochum/DE)

11^{50} **Limed clay as a replacement for construction sands**
GTA-T06 Miquel Joseph, Jelle Benoot, Luc Boehme (Oostende/BE)

12^{10} **On settlement prediction of reinforced soft clay by a group of stone columns**
GTA-T07 Seifeddine Tabchouche (Biskra/DZ), Mounir Bouassida (Tunis/TN)
Mekki Mellas (Biskra/DZ)

12^{30} **On the influence of initial permeability and stiffness on the the cyclic**
GTA-T08 **consolidation behavior of soft clays**
Nina Müthing, Tom Schanz (Bochum/DE)

12^{50} **Leaching of soil conditioning chemicals from excavated tunnel muck**
GTA-T09 Rolf Zumsteg, Michael Plötze, Alexander M. Puzrin (Zurich/CH)

13^{10} **Chemically enhanced drainage as a stabilisation technique for landslides**
GTA-T10 Pascal Minder, Michael Plötze, Alexander M. Puzrin (Zurich/CH)

Lecture hall A

11^{50}–13^{30} Analytical tools for improved characterization of clays and clay minerals II
Chair Katja Emmerich (Karlsruhe/DE)

11^{50}
ANT-T06
The determination of the cation exchange capacity with the Cu-Trien method: recommendations for improving accuracy and reproducibility
Helge Stanjek, Dennis Künkel (Aachen/DE)

12^{10}
ANT-T07
The use of modern microscopic techniques and correlative workflows in the natural resources industry
Ben Tordoff (Göttingen/DE), Andy Steinbach (Pleasanton, CA/US)

12^{30}
ANT-T08
Advanced electron microscopy techniques in characterization of clays and clay fabric
Wen-An Chiou (College Park, MD/US), Stephan Kaufhold
Reiner Dohrmann (Hannover/DE), Akira Ishikawa, Kurio Fukushima
Yuma Kuwamura, Hiroki Minoda (Tokyo/JP)

12^{50}
ANT-T09
Simulation of particle packing in swelling clay porous media
Eric Ferrage, Fabien Hubert, Emmanuel Tertre, Dimitri Pret (Poitiers/FR)
Alfred Delville (Orléans/FR), Laurent J. Michot, Pierre Llevitz (Paris/FR)

13^{10}
ANT-T10
Determination of porosity decrease function in smectite group using coupled geomechanical and phenomenological modeling
Mohsen Farrokhrouz (Shiraz/IR), Pavel Bedrikovetsky (Adelaide/AU)

Scientific Programme • Friday, 19 September 2014

Lecture hall Dresden

14^{20}–15^{20}	Clays in geotechnical applications III
Chair	Michael Plötze (Zurich/CH)
14^{20} GTA-T11	**The role of meta-clay surface area for binder materials** Jan Dietel, Laurence N. Warr (Greifswald/DE) Katja Emmerich (Karlsruhe/DE), Marko Bertmer (Leipzig/DE)
14^{40} GTA-T12	**Swelling pressure measurements in black shales with the MENARD pressuremeter** Jean-Frank Wagner (Trier/DE), Robert Heintz (Luxembourg/LU)
15^{00} GTA-T13	**Swelling inhibitors for conservation of Swiss molasse** Timothy Wangler, Michael Plötze, Robert Flatt (Zurich/CH)
15^{20}–16^{00}	Clay minerals in hydro- and geothermal systems I
Chairs	Albert Gilg (Munich/DE), Michal Skiba (Kraków/PL)
15^{20} HYD-T01	**Microwave-assisted hydrothermal synthesis of the lizardite-nepouite series and the kerolite-pimelite series** Fabien Baron, S.S.C. Pushparaj, Céline Fontaine, Matte V. Sivaiah Sabine Petit (Poitiers/FR)
15^{40} HYD-T02	**The Fe-Mg-saponite solid solution series – A hydrothermal synthesis study** Andre Baldermann (Graz/AT), Rainer Dohrmann, Stephan Kaufhold (Hannover/DE) Claudia Nickel, Ilse Letofsky-Papst, Martin Dietzel (Graz/AT)

Lecture hall B

14^{20}–15^{40} Clays, reservoir rocks and energy issues III

Chairs Reinhard Gaupp (Jena/DE), Georg Grathoff (Greifswald/DE)

14^{20} **Evolution of pore space in organic-rich mudrocks from the Hilsmulde,**
RRE-T10 **Germany – studying the influence of thermal maturity on porosity in organic particles and the mineral matrix using FIB-SEM microscopy**
Georg Grathoff (Greifswald/DE), Stephan Kaufhold
Christian Ostertag-Henning German, Matthias Halisch (Hannover/DE)

14^{40} **Effects of diagenesis and fluid interactions on the properties of potential gas**
RRE-T11 **shales**
Laura Wasch, Marielle Koenen, Tanya Goldberg, Susanne Nelskamp
Roel Verreussel (Utrecht/NL)

15^{00} **Influence of palaeoenvironment and palaeogeography on source rock potential**
RRE-T12 **and theoretical gas storage capacity of roof shales (drilling KB174, Hechtel-Hoef, Campine Basin, Belgium)**
Wim Vandewijngaerde (Leuven/DE), Kris Piessens (Brussels/BE), Bernhard Krooss
Pieter Bertier (Aachen/DE), Rudy Swennen (Leuven/DE)

15^{20} **Mineralogical changes in organic-rich Posidonia shale comparing natural with**
RRE-T13 **experimental maturation**
Julia Schlosser, Georg Grathoff (Greifswald/DE), Christian Ostertag-Henning
Stephan Kaufhold (Hannover/DE)

Scientific Programme • Friday, 19 September 2014

Lecture hall A

14^{20}–16^{00} Analytical tools for improved characterization of clays and clay minerals III

Chair Georgios Chryssikos (Athen/GR)

14^{20}
ANT-T11 **Process tomography of diffusion with PET for evaluating anisotropy and heterogeneity**
Johannes Kulenkampff, Marion Gründig, Abdelhamid Zakhnini
Johanna Lippmann-Pipke (Leipzig/DE)

14^{40}
ANT-T12 **Development of molecular cluster models for structure/property relationships of clays**
Robert Szilagyi, Robert Kurdi, Attila Taborosi (Veszprem/HU)

15^{00}
ANT-T13 **Adsorption of water to organo-montmorillonite – spectroscopic study**
Helena Pálková (Bratislava/SK), Viktor Hronský (Košice/SK), Valéria Bizovská
Jana Madejová (Bratislava/SK)

15^{20}
ANT-T14 **Terahertz time domain spectroscopy, a novel method for investigation chemically modified layered clay systems**
Marian Janek, Daniel Zich, Tomáš Zacher (Bratislava/SK)
Mira Naftaly (Teddington/GB)

15^{40}
ANT-T15 **Near-infrared study of pyridine adsorption on acid-treated montmorillonite**
Jana Madejova, Helena Palkova, Lubos Jankovic (Bratislava/SK)

Lecture hall Dresden

16^{20}–17^{40} Clay minerals in hydro- and geothermal systems II
Chairs Albert Gilg (Munich/DE), Michal Skiba (Kraków/PL)

16^{20}
HYD-T03 **Distribution of clay minerals in technological ores of the Biely vrch Au-porphyry deposit, Slovakia**
Peter Uhlík, Jaroslav Lexa, Michal Jánošík, Jana Brčeková (Bratislava/SK)
Adrián Biroň (Banská Bystrica/SK)

16^{40}
HYD-T04 **Characteristics and timing of clay mineralization in the Carboneras and Palomares Fault Zones (SE Spain)**
Isabel Abad, Juan Jiménez-Millán (Jaén/ES), Anja Schleicher
Ben Van der Pluijm (Ann Arbor, MI/US)

17^{00}
HYD-T05 **Fraipontite in the hydrothermally overprinted oxidation zone of the Preguiça mine, Southern Portugal**
Patrizia Will (Munich/DE), Frank Friedrich (Karlsruhe/DE)
Rupert Hochleitner, H. Albert Gilg (Munich/DE)

17^{20}
HYD-T06 **Genesis of hydrothermal alteration at the Kişladağ porphyry gold deposit region, Gedikler, Uşak (Western Anatolia), Turkey**
Hülya Erkoyun, Selahattin Kadir (Eskişehir/TR)

Lecture hall B

16^{20}–17^{40} Clays, reservoir rocks and energy issues IV

Chairs Reinhard Gaupp (Jena/DE), Georg Grathoff (Greifswald/DE)

16^{20}
RRE-T14 **Interaction of drilling fluids with clay minerals of northern North Sea at reservoir conditions**
Lyudmyla Wilson, Jeff Wilson, Ian Patey, Justin Green
John Maitland (Aberdeen/GB)

16^{40}
RRE-T15 **The nature and origin of the clay minerals in North Sea reservoir sandstones and their influence on formation damage**
Michael Wilson, Lyudmyla Wilson, Iain Patey (Aberdeen/GB)

17^{00}
RRE-T16 **Cation exchange capacity and water content of opal in sedimentary basins: example from the Monterey Formation, California**
Arkadiusz Derkowski, Jan Srodoń (Kraków/PL), Douglas McCarty (Houston, TX/US)

17^{20}
RRE-T17 **Effects of clay particles on the formation of methane hydrates in aqueous solution**
Diana Taylor, Neal Skipper (London/GB)

Lecture hall A

16^{20}–17^{40} Clays and clay-sized minerals in soils and young sediments III

Chair Karin Eusterhues (Jena/DE)

16^{20}
SYS-T10 **Influence of cropping practices on clay mineralogy – insights from the Morrow Plots experimental fields**
Bruno Lanson, Tauhid Belal Khan (Grenoble/FR)
Fabien Hubert (Poitiers/FR), Nathaniel Findling (Grenoble/FR)
Camille Rivard (Grenoble/FR), Michelle M. Wander (Urbana, IL/US)

16^{40}
SYS-T11 **Surface properties of micron- and submicron-sized mineral particles from modern sediments of the Adriatic Sea**
Maja Ivanić (Zagreb/HR), Srečo Kapin (Ljubljana/SI), Neda Vdović, Nevenka Mikac
Ivan Sondi (Zagreb/HR)

17^{00}
SYS-T12 **Environmental changes inferred from karst lake sediment geochemistry and clay minerals during the Holocene (Bokanjacko blato and Lake Vrana near Biograd)**
Nikolina Ilijanić, Slobodan Miko, Ozren Hasan, Koraljka Bakrač (Zagreb/HR)

17^{20}
SYS-T13 **Natural clay-sized glauconite in Neogene deposits of Belgium**
Rieko Adriaens, Jan Elsen, Noel Vandenberghe (Heverlee/BE)

Lecture hall Dresden

17^{50}–18^{30} Closing including Students awards

Poster Presentations

Overview

Analytical tools for improved characterization of clays and clay minerals

ANT-P01 **Hydration kinetics of smectites in comparison to vermiculite and illite**
Florian Schnetzer, Annett Steudel, Laure Delavernhe, Peter G. Weidler
Franz Königer, Rainer Schuhmann, Katja Emmerich (Karlsruhe/DE)

ANT-P02 **Adsorption of amino acids on ground montmorillonite**
Lukáš Petra, Peter Billik, Peter Komadel (Bratislava/SK)

ANT-P03 **Investigation of the kaolinite inner-OH and outer surface-OH with new molecular cluster model using quantum chemical methods**
Attila Táborosi, Róbert Kurdi, Róbert Károly Szilágyi (Veszprém/HU)

ANT-P04 **Hydration properties and interlayer structure of di- and tetraoctylammonium-montmorillonite**
Valéria Bizovská, Jana Madejová, uboš Jankovič (Bratislava/SK)

ANT-P05 **Application of inverse gas chromatography for the characterization of clay mineral surfaces**
Zsirka Balázs, Erzsébet Horváth, János Kristóf, Zsuzsa Járvás
András Dallos (Veszprém/HU)

ANT-P06 **Water soluble ions in non-marine bentonites (Bavaria, Germany)**
Mathias H. Köster, Dominik Stumpp, H. Albert Gilg (Munich/DE)

ANT-P08 **Interaction of selected organic molecules with immobilized Cu2+ cations in montmorillonite**
Anna Brtanova, Marian Valko, Peter Komadel (Bratislava/SK)

ANT-P09 **Pillared montmorillonites as catalysts for removal of chlorinated volatile organic compounds from air – textural characterization**
Krzysztof Bahranowski, Adam Gaweł, Agnieszka Klimek, Jakub Matusik
Alicja Michalik-Zym, Ewa Serwicka, Ewa Wisła-Walsh
Wojciech Włodarczyk (Kraków/PL)

ANT-P10 **Different tools for the investigation of micro fabric and damage patterns in claystones (Opalinus Clay, Mont Terri)**
Annette Kaufhold, Werner Gräsle, Ingo Plischke, Matthias Halisch (Hannover/DE)
Frieder Enzmann (Mainz/DE)

ANT-P12 **Characterization of functionalized PCH composites derived from Laponite**
Malgorzata Zimowska, Jacek Gurgul, Joanna Olszowka, Kazimierz Latka
Robert P. Socha (Kraków/PL)

ANT-P13 **Synchrotron X-ray scattering and Monte Carlo simulations of structure and forces in silicate nanoplatelet dispersions**
Mo Segad, Bo Jönsson, U. Olsson (Lund/SE), B. Cabane (Paris/FR)

Clay minerals in diagenetic and low temperature metamorphic environments

VLG-P01 **On the measurement of the Kübler index**
Hejing Wang, Jian Zhou (Beijing/CN)

Clay minerals in hydro- and geothermal systems

HYD-P01 **3D correlation of chemical elements (K, Ca, Na, Mg, Fe, Al) with recorded mineral composition and alteration zones at Biely vrch porphyry Au deposit, Slovakia – preliminary results**
Michal Jánošík, Peter Uhlík, Jana Brčeková (Bratislava/SK)
Adrián Bíroň (Banská Bystrica/SK), ļubica Puškelová (Bratislava/SK)

HYD-P02 **Glauconitic laminated crusts caused by hydrothermal alteration of lower Jurassic pillow-lavas mediated by microbial activity**
Isabel Abad, Matías Reolid (Jaén/ES)

HYD-P03 **Clay mineralogy in Bahariya area, Egypt: Hydrothermal implications on fault-related iron ore deposits**
Adel Mady Afify, Xabier Arroyo, Maria Esther Sanz-Montero
Jose Pedro Calvo (Madrid/ES)

HYD-P04 **Mineralogy and geochemistry of mineralizations related to subsequent alterations in the Tekirova Ophiolite Nappe, Antalya, Turkey**
Hüseyin Yalçın (Sivas/TR), Ömer Bozkaya (Denizli/TR), Canan Yılmaz (Sivas/TR)

Clays and clay-sized minerals in soils and young sediments

SYS-P01 **Clay minerals in the sediments from the Croatian Adriatic shelf**
Darko Tibljas, Kristina Pikelj, Nina Trinajstic (Zagreb/HR)

SYS-P02 **Interaction of clay and iron minerals with bacteria during soil and sediment bioleaching and metals releasing**
Darina Styriakova, Iveta Styriakova (Kosice/SK)

SYS-P03 **Origin of the neoformation minerals in the Çayırhan (Beypazarı-Ankara) volcano-sedimentary lacustrine basin,central Anatolia, Turkey: Preliminary results**
Abidin Temel, Özgül Sönmez (Ankara/TR)

SYS-P04 **Clay assemblage of sediments from southerwestern and southern sections of Portugal continental shelf**
Ana Quintela, Denise Terroso, Cristiana Costa, Paulo Costa
Fernando Rocha (Aveiro/PT)

SYS-P05 **Interactions between microorganisms and ferrihydrite-organic matter associations**
Karin Eusterhues, Anke Hädrich, Julia Neidhardt, Kirsten Küsel
Kai Uwe Totsche (Jena/DE)

SYS-P06 **Bacteriological investigation of soils under the anthropogenic influence in Croatia**
Goran Durn (Zagreb/HR), Jasna Hrenović (Zagreb/HR)
Ivana Goić-Barišić, Ana Kovačić (Split/HR)

SYS-P07 **Complex studies of clay minerals in the Yenisey river**
Anatoly Mashukov, Alla Mashukova, Svetlana Bistryakova
Svetlana Ponomareva (Krasnoyarsk/RU)

SYS-P08 **The role of soil mineral composition in defining Istrian terroir attributes**
Goran Durn, Marta Mileusnić, Elizabeta Tomašić (Zagreb/HR), Franz Ottner
Karin Wriessnig (Vienna/AT)

SYS-P09 **Mineralogical investigation of authigenic aluminum solid phases in acid-stressed forest soils of the Saarland (Germany)**
Tilo Bolken, Georg H. Grathoff (Greifswald/DE)

SYS-P10 **Qualitative and quantitative properties of clay minerals in salt-affected sediments with different organic matter and salt content in the Lake Fehér in Szeged and Kardoskút**
Gábor Bozsó, Nóra Czirbus, Magdolna Hetényi (Szeged/HU)

Clays in geotechnical applications

GTA-P01 **Amount of water in saturated compacted bentonite samples at various temperatures**
Lucie Hausmannova, Radek Vasicek (Prague/CZ)

GTA-P02 **Adobe material of the Sun Temple, Pachacamac, Peru – Engineering, geological classification as a challenge**
Renata Adamcova (Bratislava/SK), Franz Ottner, Karin Wriessnig (Vienna/AT)

GTA-P03 **The possibility of using non-qualified clay-rich sand by overview the standard (methylene blue test), mineralogy of aggregates, and engineering behavior**
Chi-Wei Chen, Myriam Duc (Champs-sur-Marne/FR)
Yannick Descantes (Bouguenais/FR)

GTA-P04 **Stabilization-potential of bentonite-polymer-mixtures and its use for landfill technology**
Hanna Dehn, Hanna Viefhaus, Tom Schanz (Bochum/DE)

Clays, reservoir rocks and energy issues

RRE-P01 **CO_2/clay interactions and the significance for geological storage of carbon dioxide**
Andreas Busch, Rick Wentinck (Rijswijk/NL), Pieter Bertier (Aachen/DE)

RRE-P02 **Structural diagenesis of an Upper Carboniferous Tight Gas Sandstone reservoir analogue**
Yasar Manß, Patrick Wuestefeld, Christoph Hilgers (Aachen/DE)
Bastian Koehrer (Barnstorf/DE), Pieter Bertier (Aachen/DE)

RRE-P03 **Definition of shale minerals in reservoir area using geochemical sampling**
Mohsen Farrokhrouz, Mohammad Reza Asef (Shiraz/IR)

RRE-P04 **Identification of clay minerals in the Cheleken reservoir series in South Caspian and appropriate drilling mud selection**
Soheyla Aslani, H. R. Samim-Bani Hashemi, Hamed Haghi, Mohsen Farrokhrouz
Alireza Jahanpanah (Tehran/IR)

RRE-P05 **Clay-mineral composition of black shales from the Dniepr-Donets Basin (Ukraine)**
David Misch, Eva Wegerer, Lorenz Scheucher (Leoben/AT)

Crystal structure of clay minerals

CRY-P01 **Intercalation of cationic polyelectrolytes into swollen vermiculites**
Diana Taylor (London/GB)

CRY-P02 **Rietveld refinement of structural parameters of dioctahedral smectites**
Xiaoli Wang, Reinhard Kleeberg (Freiberg/DE), Kristian Ufer (Hannover/DE)

CRY-P03 **Montmorillonite intercalated with tetraethylammonium cation– DFT and IR study**
Eva Scholtzová, Helena Pálková, Jana Madejová (Bratislava/SK)
Daniel Tunega (Vienna/AT)

CRY-P04 **Indexing theoretical Al-Si distribution in layer silicates – Unit cell model for generality**
Donghoon Chung, Yungoo Song, Changyun Park (Seoul/KR)
Jae-cheon Shim (Cheonan-si/KR), Woohyun Choi (Seoul/KR)

CRY-P05 **Crystal structure refinement of Ge-incorporated akaganeite(β-FeOOH)**
Park Changyun, Chung Donghoon, Song Yungoo (Seoul/KR)
Kang Il-Mo (Daejeon/KR), Kim Myunghoon (Seoul/KR)

CRY-P06 **Freezing H_2O inside the tunnels of sepiolite – a cryo-NIR spectroscopic investigation**
Vassilis Gionis, Constantinos Tsiantos, Georgios D. Chryssikos (Athens/GR)

CRY-P07 **Low temperature nir spectroscopic characterization of palygorskite and indigo in synthetic maya blue**
Constantinos Tsiantos, Vassilis Gionis, Georgios D. Chryssikos (Athens/GR)

CRY-P08 **Structural rearrangements of iron in Fe-PCH composites derived from Laponite: FTIR and Mössbauer spectroscopy comparative study**
Malgorzata Zimowska, Jacek Gurgul, Kazimierz Łątka
Zbigniew Olejniczak (Krakow/PL)

General Session

GS-P01 **Mineralogical investigation of tailing materials from historic Saxonian mining sites by X-ray powder diffraction**
René Luhmer, Alexandra Gerz, Reinhard Kleeberg (Freiberg/DE)

GS-P02 **Brick kilns and clay pits of northeastern Lower Austria – history and mineralogical characteristics**
Ingeborg Wimmer-Frey, Thomas Hofmann (Vienna/AT)
Christian Ferdinand Ramml (Niederabsdorf/AT)

GS-P03 **Reactivated timings of some major faults in the Chugaryeong fault zone since the cretaceous period**
Khulganakhuu Chuluunbaatar, Yungoo Song, Donghoon Chung
Changyun Park (Seoul/KR), Il-Mo Kang, Sung-Ja Choi (Daejeon/KR)

GS-P04 **Thermodynamic stability of trioctahedral chlorites of Mg-Fe isomorphic series (by thermochemical data)**
Victoria Krupskaya, Lyubov Ogorodova, Lyubov Melchakova, Marina Vigasina
Irina Kiseleva, Igor Bryzgalov (Moscow/RU)

Poster Presentations

GS-P05 **Surface controls for the anti-inflammatory activity by naturally-occurring halloysite**
Javiera Cervini Silva, Antonio Nieto-Camacho, María Teresa Ramírez-Apán
Elba Ronquillo de Jesús, José Ascención Montoya (Col. Santa Fe/MX)

GS-P06 **Geological, mineralogical and geochemical characterization of the Miocene zeolite-bearing volcaniclastic sediments, Ankara, Turkey**
Necati Karakaya, Muazzez Celik Karakaya (Konya/TR)

Industrial clays

IND-P01 **Bacterial removal of clay and iron minerals from quartz particles**
Iveta Styriakova, Darina Styriakova (Kosice/SK)

IND-P02 **Application of agarose-layered double hydroxide nanocomposite hydrogels as adsorbent**
Toshiyuki Hibino (Tsukuba/JP)

IND-P03 **Chromium removal using organo- and bio-montmorillonites**
Cesar Fernandez Morantes, Javier Lamarra (M.B. Gonnet/AR)
Gustavo Curutchet (San Martin/AR), Rosa María Torres Sánchez (La Plata/AR)

IND-P04 **Effect of hydration of bio-clay matrices on uranium adsorption – applications in upflow columns**
Melisa S. Olivelli (San Martin/AR), Rosa María Torres Sánchez (La Plata/AR)
Birgit Schampera (Hannover/DE), Gustavo Curutchet (San Martin/AR)

IND-P05 **Mineralogical, grain-size exchangeable cations characterization of selected Portuguese clays – effects on viscosity behaviour**
Cristiana Costa, Ana Quintela, Denise Terroso, Fernando Rocha (Aveiro/PT)

IND-P06 **Basic characterization of perlite from Lehôtka pod Brehmi deposit and its surrounds (Slovakia)**
Peter Uhlík, Jaroslav Lexa, Helena Pálková, Jana Madejová (Bratislava/SK)
Peter Blišťan (Košice/SK), Valéria Bizovská (Bratislava/SK)

IND-P07 withdrawn

IND-P08 **Preparation of 2D optically active layers using beta-cyclodextrine/dyes supramolecular complexes**
Marian Matejdes, Adriana Czímerová, Marian Janek (Bratislava/SK)

IND-P09 **Study of FRET in hybrid thin films based on saponite and cyanine dyes**
Peter Boháč, Adriana Czímerová, Juraj Bujdák (Bratislava/SK)

IND-P10 **Nanoparticles of FexOy- palygorskite, efficient sorbates for pesticide removal**
Lala Setti Belaroui (Oran/DZ), Affaf Ouali, Maranzazu Peña Heras (Granada/ES)
Abdelkader Bengueddach (Oran/DZ), Alberto López galindo (Granada/ES)

IND-P11 **Mineralogical and thermal properties of kaolinite deposits from Acoculco (Mexico)**
Maite Garcia-Valles, Mariona Tarrago, Salvador Martinez (Barcelona/ES)
Teresa Pi (Mexico/MX), Pura Alfonso (Manresa/ES)
Carles Canet (Mexico/MX), Abigail Jimenez (Manresa/ES)

IND-P12 **Synthesis and characterization of taylor-made organo-clays for biotechnological applications**
Luciana Sciascia, Ilaria Calabrese, Marcello Merli, Alessandro Pavese
Maria Liria Turco Liveri (Palermo/IT)

IND-P13 **Thermally activated clays as a main binder component for producing low-CO_2 concrete**
Torsten Seiffarth, Marc Hohmann, Christian Kaps (Weimar/DE)

IND-P14 **The commercial bentonite from Kopernica (Tertiary, Slovakia): petrographical and mineralogical approach**
Krzysztof Bahranowski, Katarzyna Górniak, Tadeusz Szydłak, Adam Gaweł
Agnieszka Klimek, Anna Tomczyk (Kraków/PL), Jerzy Motyka (Niedomice/PL)

IND-P15 **Hydrotalcite/montmorillonite nanocomposite**
Ewa Serwicka, Alicja Michalik-Zym, Daria Napruszewska, Elżbieta Bielańska
Agnieszka Klimek, Adam Gaweł, Krzysztof Bahranowski (Kraków/PL)

Properties and processes at the aqueous interface of clay minerals

PAI-P01 **The impact of EC and pH on the the adsorption of Zn and Cd by palygorskite mineral**
Ibrahim Alhawas (Alhasa/SA)

PAI-P02 **Electrokinetic potentials, surface conductivity and cation exchange capacities from the electrical conductivity of kaolinite suspensions**
Christian Weber, Helge Stanjek (Aachen/DE)

PAI-P03 **Removal of chromate, arsenate and phosphate oxyanions by halloysite from Dunino deposit, Poland**
Anna Prokop, Jakub Matusik (Kraków/PL)

PAI-P04 **Interactions of clay-based pigments with organic binders**
Vlasta Vasutova, Petr Bezdička, Janka Hradilová, David Hradil (Praha/CZ)

PAI-P05 **Hybrid material based of kaolinite and rhodamine B**
Samuel Sas, Martin Danko, Juraj Bujdák (Bratislava/SK)

PAI-P06 **The role of clay minerals in the metal sorption in soils as studied by analytical transmission electron microscopy**
Peter Sipos, Tibor Nemeth, Viktoria Kovacs Kis (Budapest/HU)

PAI-P07 **A study of phosphate removal by calcium–iron layered double hydroxydes**
Muayad Al-jaberi, Christian Ruby, Sébastien Naille (Villers-lès-Nancy/FR)

PAI-P08 **Comparison of interactions between montmorillonite surface and organic species**
Miroslav Pospisil (Praha/CZ)

PAI-P09 **Zeta potential and antimicrobial activity of biodegradable chitosan/bentonite nanocomposite**
Mehmet Cabuk (Isparta/TR), Yusuf Alan (Mus/TR)

PAI-P10 **Particle size and shape analysis of clays using electron microscopy**
Wen-An Chiou (College Park, MD/US), Stephan Kaufhold
Reiner Dohrmann (Hannover/DE)

PAI-P11 **Adsorption of cadmium, chromium and lead cations on north-patagonic clay minerals**
Graciela Mabel Silva (Neuquén Capital/AR)
Silvia Graciela Acebal (Bahía Blanca/AR), Rosa María Torres Sánchez (La Plata/AR)

PAI-P12 **Using of Fe-modified kaolines for decontamination of areas polluted by toxic oxyanions (As, Sb, Se)**
Petra Houdková, Barbora Doušová (Praha/CZ)

PAI-P13 **Using of synthetic aluminosilicates for removal phosphates from aqueous environment**
Lenka Holcova, Barbora Doušová (Prague/CZ)

PAI-P14 **Effect of cyclic wetting and drying on swelling and non-swelling clay minerals**
Tibor Németh (Budapest/HU)

PAI-P15 **Evolution of rheological properties of sodium montmorillonite dispersions near the sol-gel transition point**
Boris Pokidko, Pavel Surikov (Moscow/RU)

PAI-P16 **Influence of bentonite on sorption of organic compounds in groundwater aquifer**
Miroslav Holubec, Marian Matejdes, Adriana Czímerová (Bratislava/SK)

PAI-P17 **Kaolinites: Ordering-disordering and adsorption properties**
Olga Dorzhieva, Viktoria Krupskaya, Sergey Zakusin, Boris Pokidko
Daria Kurmasheva, Vasily Artemov (Moscow/RU)

Stability of engineered clay barriers in radioactive waste disposal

RWD-P01 **Alteration of nanocrystalline calcium silicate hydrate (C-S-H) at pH 9.2 and room temperature**
Nicolas Marty, Sylvain Grangeon, Fabienne Warmont
Catherine Lerouge (Orléans/FR)

RWD-P02 **Correlation between mechanical properties of the bentonite and its swelling behavior**
Dubravko Domitrovic, Biljana Kovacevic Zelic, Zelimir Veinovic (Zagreb/HR)

RWD-P03 **Effects of chemical structure on stability of smectites in short-term alteration experiments**
Nguyen Thanh Lan, Horst-Jürgen Herbert, Jörn Kasbohm, Thao Hoang-Minh
Rafael Ferreiro Mählmann (Darmstadt/DE)

RWD-P04 **Bentonite pellets for use as gap filling**
Jiri Stastka (Prague/CZ)

RWD-P05 **Preparation of Slovak HDTMA-bentonite for U(VI) adsorption study**
Adrian Krajnak, Eva Viglasova, Michal Galambos, Olga Rosskopfova
Renata Adamcova (Bratislava/SK)

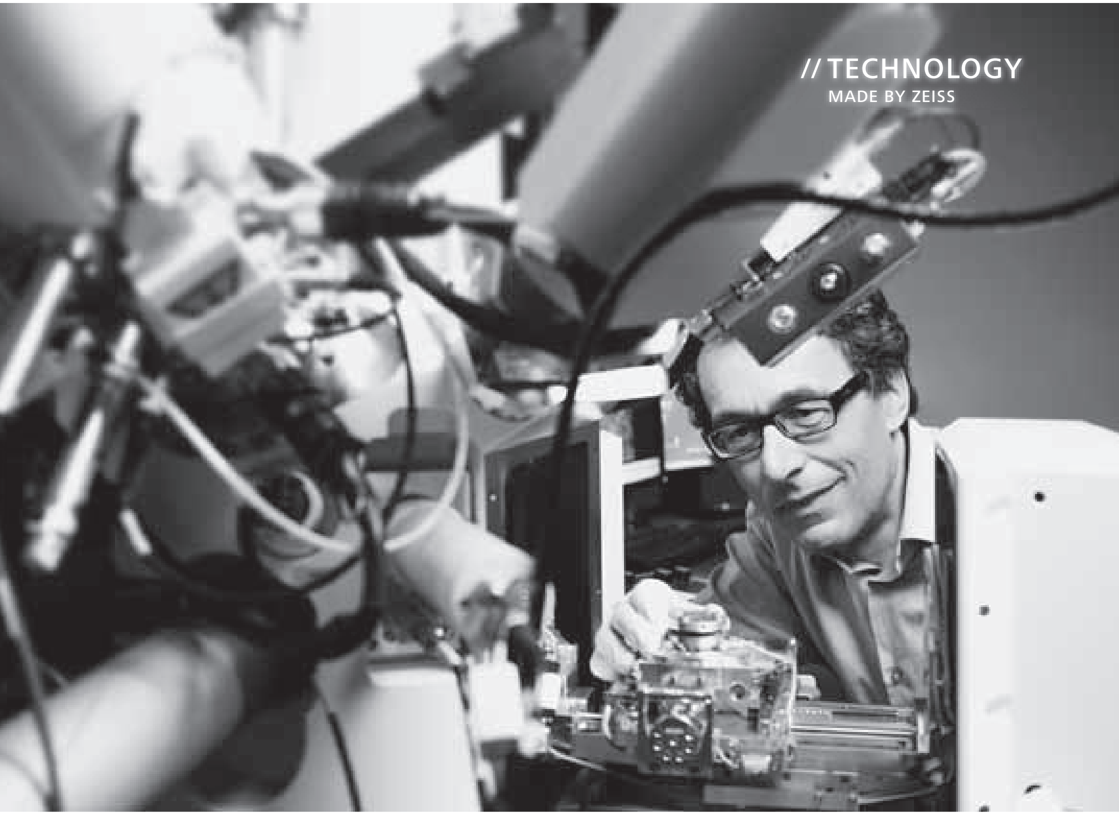
RWD-P06 **Na-montmorillonite microstructure**
Michał Matusewicz, Andrew Root, Jussi-Petteri Suuronen (Helsinki/FI)
Markus Olin (Espoo/FI)

RWD-P07 **Bentonite erosion and colloid mediated transport of radionuclides in advection controlled systems**
Franz Rinderknecht, Stephanie Heck, Robert Götz, Johannes Laber, Florian Huber
Thorsten Schäfer, Horst Geckeis (Karlsruhe/DE)

RWD-P08 **In-situ study of bentonite interaction at temperature up to 95 °C**
Milan Zuna, Jarmila Pospíšilová, Michal Vaněček, Pavel Bílý, Jana Kasíková
Petr Novák, Martin Šťastný, Jiří Stástka, Jan Franěk, Jan Holeček
Jan Najser (Prague/CZ)

RWD-P09 **Monte Carlo and Molecular Dynamic simulations addressing the tactoid formation and swelling of charged clay platelets**
Axel Thuresson (Lund/SE)

RWD-P10 **Alteration of clay minerals under the influence of acid solutions that accompany radioactive wastes**
Sergey Zakusin, Viktoria V. Krupskaya, Olga V. Dorzhieva
A. P. Zhukhlistov (Moscow/RU)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Index of Plenary Speakers and Presenting Authors

Abstracts

The physical meaning of clay mineral indices and reaction progress in pelitic rocks

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The application of transmission electron microscopy (TEM) techniques to geomaterials over the last decades has advanced our knowledge of the physical entities behind many phenomena, interpretations and concepts previously inferred from indirect methods. Clay minerals, due to their poorly crystalline nature, have particularly benefited from such combined analytical approaches. Lattice fringe images reveal the size, distribution and texture of individual packets of phyllosilicates and the sequence of alternation of the various layers that form interstratified structures. Selected area electron diffraction also resolves the usual information obtained by X-ray diffraction but at the level of individual grains, rather than on bulk powders, and analytical electron microscopy is able to determine chemical composition similarly at the same local scale. In most cases, TEM studies have verified the classical models inferred by X-ray diffraction (XRD) and related techniques, such as confirming the physical nature of ordering in mixed-layer clay minerals or the validity of calculating the average crystalline domain size by the Scherrer equation. Nevertheless, even for such well studied phenomena, TEM can reveal complementary information concerning the inherent nature of nanosized structures and provide observations on the genetic meaning of microstructural differences. For example, the average domain size is the main determining factor of the Kubler Index (KI) but this size is only a statistical expression of highly scattered and potentially complex size distributions, which may include variations of more than one order of magnitude in measured dimensions. The average size of such domains has been shown to be the predominant factor in epizone and anchizone pelitic rocks, where crystalline defects become less frequent and smectitic layers are virtually absent. However in deep diagenetic rocks, TEM studies reveal that the broader KI values are in addition to domain size also strongly influence by the proportion of smectitic interlayers present, which is an integral part of its physical meaning. The differential effects of these two physical causes of peak broadening may be evaluated by comparing the traditional expression of the KI with equivalent measures carried out on the 5 Å peak and/or by comparing air-dried and glycolated samples, or with the help of peak decomposition procedures. In addition to that of KI, the physical meaning of mica polytype ratios and interstratified clay mineral parameters can also be refined by further TEM investigations.

Simulation of XRD patterns of clay mineral defective structures

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High dispersion, presence of various defects, structural and chemical heterogeneity are typical features of clay minerals. Implicitly, the information about these features is contained in the positions, intensities and profiles of peaks in X-ray diffraction (XRD) patterns. Simulation of experimental XRD patterns is one of the effective techniques for the determination of structural information from these minerals. Both the structural parameters of a model and instrumental factors, all having definite physical meaning, are required for modeling experimental XRD patterns. Moreover, there should be a set of models that comprise all the diversity of the structural features of natural clay minerals. They should have no limitations in:

- number and distribution of layer types or stacking faults at a given short-range order factor
- variability of atomic coordinates and their occupancies in unit cells
- presence of layer-thickness or *ab*-translation fluctuations
- difference between structures of outer and core layers
- different shape and size distribution of coherent scattering domains, etc.

Due to the low sensitivity of diffraction to different types, contents and distributions of defects several structural models may often provide equally close agreement between calculated and experimental patterns. The most reliable structure is obtained by the multispecimen approach, in which XRD patterns of a clay sample subjected to different treatments (e.g. saturation by Ca, Mg, Na or K) and recorded in different states (e.g. air-dried, glycolated or heated) are successfully modeled in terms of the same statistical model. If, for some reason, the application of the multispecimen approach is restricted, the results of the study of the same sample by other physical methods (chemical, spectroscopic, electron diffraction, etc.) should be mutually consistent with those obtained by XRD modeling. It is shown that this technique has revealed a new diversity in the structure, composition and heterogeneity of layer silicates and clay minerals, provided new insight into the structural mechanisms of their formation and transformation in different geological environments, and discovered new natural processes.

Hybrids based on organic dyes and smectites – fundamentals and potential applications

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This presentation summarizes several aspects of dye / smectite interactions. Dyes adsorbed on clay particles frequently form molecular aggregates and can dramatically change their color. When this phenomenon was described for methylene blue/clay colloids for the first time, smectite effect on the dye aggregation had not been fully understood. The type, structure and photophysical properties of dye aggregates do not always fully correlate with the type or structure of the mineral. The mystery was solved after the effect of layer charge was discovered. Since then, dye molecular aggregation has been used several times for the estimation of the layer charge of smectites. The method is applicable to sensitively detect very small changes of the layer charge upon the chemical treatment or for the detection or determination of smectites in aqueous systems with sub-ppm concentrations. Using a template of appropriate clay, one can sensitively control the structure and the properties of adsorbed dye aggregates. It has opened new challenges in materials chemistry. New types of hybrid materials have been developed exhibiting the properties of light anisotropy, luminescent solids, photosensitizers, materials for light energy absorption, manipulation and controllable transfer. Using clay minerals it is now possible to stabilize some dyes against decomposition or photoisomerisation. In other cases, one can induce structural changes of dye molecules or promote their decomposition. Some of the findings in dye/clay chemistry are perspective for industrial applications, especially more complex systems based on organoclays or layer-by-layer assemblies.

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0291-11 and Grant Agency VEGA (2/0107/13, 1/0943/13).

“Vermiculite” – What a mixture!

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The term vermiculite is used in a variety of different ways. Familiar to many will be its use as an industrial commodity term to describe commercially exploited deposits of micaceous minerals which can be exfoliated when heated rapidly to high temperatures. Exfoliation involves a volume expansion with individual platy particles expanding in an accordion-like fashion to up to 20-30 times their original volume. In their exfoliated form, the accordions of vermiculite resemble worms explaining the origin of the name ‘vermiculite’. Historically, any mineral that exfoliated when flash heated was identified as vermiculite. In the mineralogical sense, vermiculite is a precisely defined name for a group of 2:1 phyllosilicates with a layer charge of between 0.6 and 0.9 per $O_{10}(OH)_2$. Vermiculites may be dioctahedral or trioctahedral. Although it appears that macroscopic, and certainly all commercially exploited deposits, are trioctahedral, whereas soil vermiculites are often dioctahedral. Thermal exfoliation has been related to the rapid production of steam during flash-heating which forces open the layers of vermiculite as the steam escapes from the structure. However, a completely satisfactory explanation for the mechanism of exfoliation has not yet been offered. The present talk describes an adventure to elucidate the mechanism of exfoliation of ‘Vermiculite’. Exfoliation is related to a mixed mosaic distribution of different mineral phases within the particles. Lateral phase boundaries between vermiculite and mica layers, or vermiculite and chlorite layers are postulated to impede the escape of gas from a particle, resulting in exfoliation when the pressure exceeds the interlayer bonding forces. This mechanism provides a common explanation for the exfoliation of ‘Vermiculite’ by thermal methods or by treatment with H_2O_2. Paradoxically, pure vermiculite does not exhibit the property of exfoliation. The mechanism explains the commonly observed particle size dependence of exfoliation and the tendency for obviously poly-phase ‘Vermiculite’ samples to show the largest coefficients of expansion. Clearly ‘vermiculite’ is an interesting mixture, and the perspective gained is one that is also relevant for studies of soils.

What do experiments tell us about the rate of reaction in the real world?

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Experimentally determined rates of reactions in diagenesis can be several orders of magnitude (maximum 5?) above those determined from studies of natural systems. Evidence for rapid growth in diagenetic systems is rare, but might include the fibrous morphology of illite as common observed within deeply buried sandstones. This requires that growth must out-strip the diffusive or advective supply of ions. Even here, there is evidence of progressive alteration of the illite fibres once formed, on a time scale of 10’s millions of years: illite from the UK Northern and Central North Sea has systematically increasing K-content with present day burial depth, but not with the estimated depth of initial formation. An examination of the chemistry, thickness and length/width distribution of separated illite fundamental particles suggest alteration of illite after initial crystal growth, potentially by Ostwald ripening over 10’s of millions of years of progressive burial (Wilkinson et al., 2014).
The rates of mineral reactions are used within computer models to predict the extent of reaction between artificially injected CO_2 and the fluid/host rock system in Carbon Capture and Storage (CCS). Published examples of computer models of CO_2 injection during CCS often suggest that a high proportion of the CO_2 will react with the rock and form stable carbonates minerals within a few decades, and as such cannot escape into the atmosphere and contribute to climate change. However, studies of natural analogues of CO_2 storage suggest that, even after geological periods of time, only a relatively small proportion of the CO_2 will have reacted to form solid minerals, e.g. 6 - 24% in the UK Miller oil field. The discrepancy between the experimentally-calibrated models, and the long-term natural analogues is difficult to reconcile - unless the silicate (including the clay mineral) fraction of the rock holds the key? Buffering of pH by the silicate minerals may take 10’s millions of years.

Analytical tools for improved characterization of clays and clay minerals

Quantitative mineral analysis of complex mineral assemblages – the Reynolds Cup round robins of the CMS in clay analysis

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The quantification of clays with phases having stacking faults like turbostratic disorder (e.g. smectite), with interstratified minerals (e.g. I/S), and with their strong tendency to preferred orientation in sample preparation has been always a big problem. The traditional methods like internal standard or RIR do not provide a satisfactory solution and also the Rietveld method is not able to fit the pattern with the same accuracy as for other phases.

In 2000 the Reynolds Cup, a biennial competition in quantitative mineral analysis was established. The Cup is supported by the Clay Minerals Society and open to anyone interested in quantitative mineral analysis with particular emphasis on clay mineralogy. The main goal is to promote and improve quantitative mineral analysis but in a sportive spirit! Unlike in other round robins, mixtures of pure mineral standards that represent realistic sedimentary rock and soil compositions were used. Although the choice of analytical approaches is free the most commonly applied method is the XRD with Rietveld analysis.

The presentation deals with developments in analytical approaches in the decade of the Reynolds Cups. Results of the last (the 7th) Reynolds Cup will be reported including specialties of the provided mixtures and details of their preparation as well as the analytical techniques used by the participants particularly those used by the top three contestants.

Identifying and fixing methodical weaknesses by participating the Reynolds Cup competition in quantitative mineral analysis

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The Reynolds Cup does not only pose a scientific challenge for mineralogists but offers also an independent sight on the weaknesses of the techniques applied in an individual laboratory. Some of the errors seem to be related to well known problems, but nevertheless these mistakes are common in routine as well as in intensive competitive analytical work. The aim of this talk is to highlight problems of mineral analysis using the data of the 7th Reynolds Cup competition. Some exemplary conclusions will be drawn and ideas for methodic improvements will be drafted.

Qualitative identification of minor non-clay minerals in complex mixtures by X-ray powder diffraction techniques is known to be limited due to low peak intensity and peak overlap. Successful strategies are (i) applying mineral enrichment or even single grain separation for XRD and SEM, (ii) performing low-noise measurements, (iii) applying peak identification from difference plots of preliminary Rietveld refinements, and (iv), more unconventional, running measurements on just coarsely powdered samples to enhance peak intensities. Such techniques were successfully applied to identify of <1 wt% of tourmaline in samples 1 and 3 as well as for the identification of amphibole and its compositional constraint. On the other hand, SEM-EDX analysis can give valuable information for the presence of phases which could not be identified in any XRD pattern, as demonstrated for apatite and nahcolite.

The correct identification of clay minerals from basal reflections measured on oriented samples seems to be straightforward, but practical limitations arise from the limited amount of sample, complicating the application of standard particle size separation techniques. Nevertheless, it is important to apply standard procedures commonly used in clay mineralogy like controlling the interlayer cation occupation, as demonstrated by the improved detection limit for I/S in sample 2.

In fact all quantification procedures successful in the RC competition are based on XRPD patterns but suffer from profile overlap. Especially, the differentiation of disordered 2:1 minerals needs for improved modeling of the diffraction profiles, including the basal reflections in randomly oriented samples. Some minerals call for the application of other techniques than XRD.

Parametric Rietveld refinement of coexisting disordered clay minerals

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X-ray powder diffraction (XRD) in combination with the Rietveld method became one of the most common methods used for quantitative analysis of phase mixtures like geologic samples. The correct application requires a complete identification of all phases and the choice of adequate structure models. This becomes laborious and time-consuming for large sample series which contain a high number of phases or minerals with similar structures like layer silicates. The expense of time increases even more if disordered clay minerals are present due to the high computational effort. It will be demonstrated here for a series of drilling core samples from a potential gas shale that the time and work expense can be reduced by a statistical assessment of supporting analysis like XRF data or fast overview XRD measurements. The definition of groups of samples with a similar composition and the identification of representative samples or outliers allow to reduce the number of detailed examinations to characterise the whole sample series.

The correct identification and choice of structural models for coexisting disordered clay minerals is difficult. It will be shown that the use of a structure model which is too general or even inappropriate has a small impact on the determination of the overall clay content. On the other hand the correct choice of the disorder model for the refinement of structurally significant parameters is essential. Even the application of correct models for coexisting disordered minerals may lead to non-unique results, due to the correlation of structural parameters.

One way to reduce the number of refineable parameters is the parametric Rietveld refinement [1]. The sample will be measured with different pre-treatments (e.g. different intercalations), different temperature or relative humidity, and/or different experimental setup (powder or oriented samples). All patterns will be fitted in one overall refinement process by the connection of the structural models via external parameters. Even the stratigraphic belonging of geological samples can be interpreted as connecting parameter. The capabilities and limitations of this approach are demonstrated on mixtures of reference materials and simulated data.

[1] Stinton, G.W. & Evans, J.S.O. (2007). J. Appl. Cryst., 40, 87-95.

Characterization of synthetic trioctahedral smectites with X-ray diffraction – an attempt to evaluate smectite heterogeneity

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Until recently, characterization of trioctahedral smectites by XRD methods included merely identification of the trioctahedral character, from the position of the 060 diffraction maximum. Recently we proposed a simple method based on XRD to identify trioctahedral smectites[1], which includes a) heating at 500 °C and subsequent EG-solvation and b) Cs-saturation and glycerol solvation. We applied the method to 4 synthetic Li-hectorites with layer charge 0.4-1.0 e/huc and 2 Na-hectorites with charge 0.5 e/huc and with and without annealing[2,3]. The Li-hectorites are Li-hectorite/Li-stevensite mixtures, with stevensite decreasing with increasing layer charge and disappearing at 1.0 e/huc (Li1.0). Li1.0 consists of Li-hectorite, a phase forming a 15.4 Å EG-complex, and an R1 mixed layer phase of these two members. The air-dried (AD) Li-hectorites contain double layer and single layer water complexes, with the former dominating in Li0.4, Li0.6 and Li0.8 and the latter dominating in the Li1.0. The Cs-saturated, glycerol solvated hectorites displayed increasing swelling with increasing layer charge, in accordance with the hydration behaviour[2]. This finding, is opposite to the expected reversed relationship between layer charge and crystalline swelling and is explained by the concept of fundamental particle charge[4]. The Na-hectorites are mixtures of hectorite and stevensite, with the latter almost disappearing in its annealed counterpart (Na0.5 Ann). Hence annealing eliminated octahedral vacancies. The AD Na-hectorites are dominated by single layer complexes. The Cs-saturated hectorite did not swell in glycerol vapours whereas the annealed sample consisted of incomplete single layer complexes, double layer complexes and non swelling complexes, the latter being dominant. The annealed sample contains also an R1 mixed layer phase, consisting of fully expandable layers and non swelling layers (d_{001} 28.4 Å). The observed swelling behavior of the Na0.5 Ann is also compatible with the concept of fundamental particle charge.

[1] Christidis, G.E. & Koutsopoulou, E. (2013) Clay Miner., 48, 687-696.
[2] Kalo, H et al (2012). Nanoscale, 4, 5633-5639.
[3] Stöter et al (2013) Langmuir, 29, 1280-1285.
[4] Pratikakis, A. et al. (2010) SEA-CSSJ-CMS Meeting, Seville, Abstracts. 154-155.

Fully automated TIC/TOC and TS analysis in clay and related matrices by multi EA® 4000

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The determination of inorganic (TIC) and organic (TOC) carbon species as well as sulfur content (TS) is crucial, e.g. to estimate the calcium content in different phases of soils. Various techniques are known to quantify these parameters but most are laborious and therefore not practical, esp. with large amount of samples. The multi EA® 4000 offers fully automated determination of the carbon species as well as simultaneous measurement of the sulfur content. With this analyzer a quantity of further applications are available, e.g. monitoring of weathering effects, evaluation of pedogenesis, and quantification of elemental carbon. The high dynamic range of the installed NDIR detectors in combination with the possibility to weigh in up to 3 g of matter offers the possibility to analyze samples of various carbon and sulfur contents (from 0 – 100%). Designed for solid samples it is an ideal tool for straightforward quantification of these parameters in dried and ground clay samples, other soils, or sediments.

Figure 1. The multi EA® 4000

The determination of the cation exchange capacity with the Cu-Trien method: Recommendations for improving accuracy and reproducibility

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The Cu-Trien method is a frequently used method to determine the cation exchange capacity of smectites, because it is a fast and technically simple method (Meier & Kahr, 1999). In practice, however, the method suffers from yet unknown error sources, which reduces its reliability (Dohrmann et al. 2012). In our study we observed, e.g., reproducible dependencies of the cec with varying ratios of sample to Cu-Trien. Additionally, pH series showed cec variations not in line with theoetical expectations. We identified the protonation behaviour of both uncomplexed and complexed trien molecules as the major source of errors. We will show that the apparent charge of the Cu-trien complex varies with pH and, thus, is probably the major source of variations. We provide a correction function for improving the accuracy of the method.

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The use of modern microscopic techniques and correlative workflows in the natural resources industry

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Automated mineral analysis has developed from a processing tool in the mining industry to a workhorse in the oil & gas industry due to the ability to now provide a full quantitative analysis in workable timescales. The use of quantitative EDS to provide a mineral identification is independent of system and matrix effects and the user does not require knowledge of the sample composition prior to analysis. This development has significantly increased the validity of automated mineralogy systems for use in the oil & gas industry where the sample composition is unpredictable.

On a parallel development path, 3D X-Ray microscopy is now capable of both high throughput mineral discrimination and the imaging of fluid flow through reservoir rocks at, or close to, reservoir conditions.

Combining both datasets begins to bridge the gap between macroscopic and microscopic rock properties. The combination of these methods can uniquely improve reservoir modelling and lead to higher accuracy in digital rock physics simulations. This talk provides examples of the use of these techniques to better predict reservoir behaviour.

Advanced electron microscopy techniques in characterization of clays and clay fabric

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Characterization of clay and clay fabrics is crucial to clay research but difficult to accomplish due to miniscule particle size, diversity in shapes, high surface activities, and limited sample preparation methods. The high resolution imaging afforded by electron microscopy makes it a powerful methodology in clay research. This paper presents three novel methods of advanced modern electron and ion beam instrumentation (wet environmental-cell TEM, TEM tomography, and advanced focused ion beam) that address these challenges in studying clay minerals and fabric.

Special techniques have been developed to overcome the difficulty of clay specimen preparation in their natural state. The wet environmental-cell TEM (WETEM) technique provides a special wet environment chamber at near atmospheric pressure in TEM that allows for examination of individual clay particles in a liquid environment at high resolution. Clay particles of different shapes that are atypical in conventional TEM and SEM are found in WETEM. The cryo-method involved creates a thin vitrified film of clay suspensions using a specially designed cryo-plunge device, and is capable of preserving different clay particle size and orientation before settling occurs. Recent developments of the high tilting TEM sample holder and sophisticated TEM tomography software allow for spatial distribution and viewing of the particle-to-particle relationships in 3D at high resolution. The advanced focused ion beam (FIB) technique provides opportunities to study both the morphology and microchemistry of clays and clay fabrics in layer by layer fashion. Using this technique, samples at nearly atomic thickness can be acquired; additionally, useful data can be recorded during the slicing process by using the e-beam. The series images and X-ray spectrum can then be reconstructed to 3D stereographs for further study. Examples of application using the aforementioned techniques will be presented.

Simulation of particle packing in swelling clay porous media

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The anisotropic properties of water and solutes migration in natural systems containing swelling clay minerals (smectite or vermiculite) is most often driven by the mutual arrangements of their lamellar particles which induce an anisotropy in the pore space morphology and connectivity of the porous media. In this scope, the simulation of representative porous media for swelling clay minerals is crucial to attempt to relate the shape of particles with their organization in the porous media and in fine to determine the dynamical properties of water and elements (cations, anions) diffusing through. For montmorillonite, the determination of particle morphology is delicate due to its osmotic crystal swelling in water saturated conditions. In order to tackle this problem, we have been interested in the characterization of different size fractions of vermiculite (i.e., 0.1-0.2, 1-2 and 10-20 µm) obtained by sonication process (Reinholdt et al., 2013). The morphological analysis revealed a similar aspect ratio for particles in the different size fractions, despite the analysis of the degree of anisotropy in particle orientation for the different porous media showed significant size-dependency (Hubert et al., 2013).

In this study an algorithm, similar to the one proposed by Coelho et al. (1997), was used to mimic the three-dimensional organization of swelling porous media for particles having elliptic disk morphology. This algorithm describes the one-by-one particle deposition under a gravitational field according to the steepest-descent method. The obtained results showed that the experimental data, such as the distribution of particle geometric factors (surface and aspect ratio) as well as particle orientation (rocking curves), can be correctly reproduced for the three vermiculite size fractions. The obtained virtual porous media can then be used to assess the size of the representative elementary volumes as well as the size and shapes of the pores based on the chord length distribution analysis. The simulation of representative 3D virtual porous media represents a crucial step for further simulations of diffusion properties of water and solutes in these systems.

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Determination of porosity decrease function in smectite group using coupled geomechanical and phenomenological modeling

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Clay minerals, especially montmorillonite, swell in contact with water and this phenomenon is followed by instability problems and sloughing as well as rock displacement into the wellbore area. Microscopically, smectite group consists of two inward-pointing tetrahedral sheets with a central alumina octahedral sheet. As water (or precisely, cation) is absorbed into the mineral lattice, causes expansion in z direction and molecular weight increases. In addition, with changes in the volume the porosity also decreases.

In the present study, mathematical modeling of porosity decrease is the objective of the research in a shaly layer located between two coal layers and low salinity water is flowed in the wellbore area. Parameters in the modeling were ionic strength of the formation, pore pressure changes with time and induced stress while water contacts the shale. Porosity decreases as a function of chemical induced stress changes and erosion based changes. During the mathematical modeling, the partial differential equations (PDEs) were applied for each stage including mass balance equation, Darcy's law for fluid flow in the porous media and momentum balance equations. Final equations showed monotonic behavior of porosity decrease function. Besides, as an accepted experience in shale drilling, less contact time leads to more stable formation as porosity does not decrease greatly and fluid flow is present inside the formation. Using the velocity equation, the amount of displaced rock into the wellbore could be measured. The results of this research were applicable in all shaly formations inside conventional and unconventional inter-beds in the oil and gas reservoirs.

Process tomography of diffusion with PET for evaluating anisotropy and heterogeneity

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Anisotropy, compositional and structural heterogeneity of clays cause considerable deviations from homogeneous diffusion, in particular direction dependent transport rates and preferred transport zones. Conventional diffusion experiments, treating the sample as homogeneous black box in a concentration gradient, are interminable and inappropriate to elucidate these spatial effects. In contrast, tomographic imaging methods are capable both to shorten the required observation time and to reveal space-dependent variations of the diffusion process.

Here we applied positron-emission-tomography (PET) as quantitative spatiotemporal imaging method with perfect characteristics for non-destructive diffusion process observations. We adopted this nuclear medical imaging method and developed its geoscientific applicability in the past ten years [1-3]. GeoPET visualizes the concentration of certain positron-emitting radiotracers in opaque media with ultimate sensitivity (picomoles) and reasonable resolution (1 mm) on the laboratory scale (100 mm). For diffusion experiments longer living nuclides are applicable, like ^{58}Co ($T_{1/2}$=70.86 d) and ^{22}Na ($T_{1/2}$=2.603 a), and we have to consider the higher density of our specimens, which causes attenuation and scattering of the radiation [4].

GeoPET revealed spatial particularities in diffusion experiments that have been conducted on Opalinus clay samples of different sizes, as well as on other rock types. Applying the Comsol Optimization Module, we derived anisotropic diffusion parameters from the tomograms [5,6].

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Development of molecular cluster models for structure/property relationships of clays

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A common feature of clays is their periodic structure, where sheets of octahedral Al(III) and Si(IV) ions alternate. From coordination chemistry perspective, we can consider combinations of Al(III) and Si(IV) ions to define various molecular coordination spheres. For example, when adsorption properties are discussed, often a honeycomb-like unit of [6Al-6OH] or [6Si-6O] moiety is considered. Taking any of these units as inner-sphere coordination environment, a layer of outer-sphere ions can be selected to complete the coordination sphere in a chemically meaningful way. Similarly, the second outer coordination sphere can terminate the dangling bonds, unfilled valences of the first outer sphere.

A systematic computational model development is presented based on coordination chemical principles for ionic and covalent bonds. The effect of various inner and outer sphere coordination environments were evaluated and minimal requirements, optimal conditions were defined for carrying out molecular cluster calculations with density functional theory.

These models allows us to study adsorption, intercalation, delamination, transition metal ion incorporation and reactivity in clays and aid the experimental design and data interpretation.

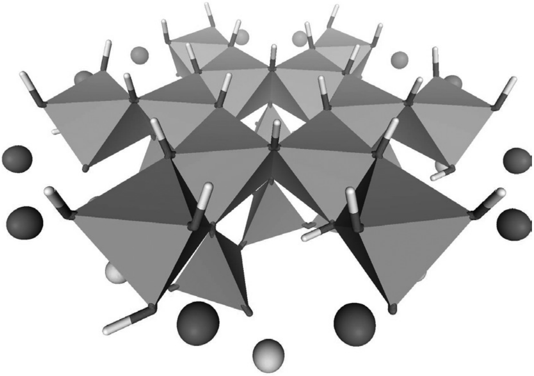

Figure 1. The octahedrally coordinated Al(III)-face of the molecular cluster model of exfoliated kaolinite

Adsorption of water to organo-montmorillonite – spectroscopic study

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Modification of a clay mineral surface with quaternary alkylammonium cations results in a material with surface properties considerably different from unmodified sample. The influence of organic cation size on the water vapour uptake by montmorillonite was examined and the comparative study with natural clay mineral was provided. The organoclays were prepared from Li-saturated SAz-1 montmorillonite (Li-S) and tetramethylammonium- (T-) or hexadecyltrimethylammonium- (H-) salts. Samples were exposed to water vapour under various relative humidity (RH) and the H_2O content was characterised by infrared and MAS NMR spectroscopies. According adsorption isotherms the amount of water decreased in order Li-S > T-S > H-S. Upon hydration the ^{1}H MAS NMR spectra showed the increase in the intensity of signals of hydrogen assigned to water molecules compare to those of structural OH groups and hydrogens present in organic cation. The hydration of montmorillonites caused also the changes in their near-infrared spectra. Presence of water in dried Li-S indicated the first $2\nu_{OH}$ overtone near 7054 cm^{-1} together with a shoulder at 6830 cm^{-1} and the combination mode $(\nu+\delta)_{H2O}$ at 5235 cm^{-1}. Reduced intensity of water bands for H-S and T-S compared to Li-S confirmed lower water content in organo-montmorillonites. Upon hydration, the intensity of both, $2\nu_{OH}$ and $(\nu+\delta)_{H2O}$ bands gradually increased, reflecting growing level of hydration. Alteration in the chemical shifts values were observed in ^{13}C MAS NMR spectra of T-S and H-S. Signal of carbon from rigid structure with $\delta = 57.3$ ppm dominated in the spectra of T-S. Hydration of the samples caused movement of the resonance towards chemical shift assigned to carbons of T^+ cation surrounded by solvent. Signals with chemical shifts of 30.8 ppm and 32.3 ppm showed coexistence of both, gauche and all-trans conformers in H-S. Upon hydration, the intensity of gauche conformers overtakes the intensity of all-trans conformers. This may indicates the influence of water on the nearest surroundings of the organic cation.

Financial support from Slovak Research and Development Agency (No. APVV-0362-10) is acknowledged.

Terahertz time domain spectroscopy, a novel method for investigation chemically modified layered clay systems

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Terahertz time domain spectroscopy (THz-TSD) was recently successfully used for the investigation of layered clay minerals in the far-infrared region. This technique enables measurement with high signal sensitivity and phase information, enabling rich spectroscopic and dielectric analysis in the range of about 0.1-3.0 THz. The details of THz-TDS measurements can be found elsewhere. Interesting differences were observed in the frequency dependence of absorption coefficient α_Samong all studied samples. The steepest rise of absorption coefficient with frequency was detected for parent HSH (72 cm^{-1} @ 1THz) and M48 (78 cm^{-1} @ 1 THz), while the weakest was shown by KBO (2.5 cm^{-1} @ 1 THz). This behavior is connected to water content present as hydration water of exchangeable cations in HSH and M48 samples, or to the differences in the chemical composition of selected samples. It was demonstrated that organic molecules such as amines and amino acids change the refraction and absorption properties of modified clay minerals upon their adsorption, despite the high absorption coefficient of the parent clay samples at the level of about 100 cm^{-1}.

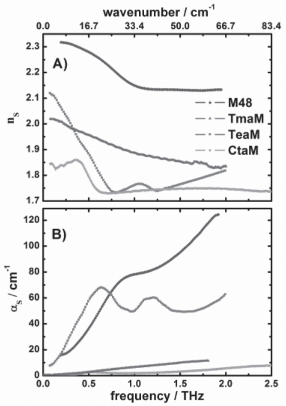

Figure 1. Dependence of refractive index n and power absorption α coefficient

Near-infrared study of pyridine adsorption on acid-treated montmorillonite

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The effect of montmorillonite structure degradation on the creation of acid siteswas investigatedby near infrared (NIR) spectroscopy using pyridine as probe molecule.Na-form of SAz-1 montmorillonite was treated in HCl for 2-8 hours. Dried samples were placed in desiccator with pyridine vapors and then the NIR spectra were measured. To examine the strength of the pyridine bonding the samples were heated at 110, 170, 230 °C prior to IR analysis. Gradual decrease of the intensities of the bands related to structural OH groups reflected release of the octahedral atoms from Na-SAzupon HCl attack. New band near 7315 cm^{-1} due to SiOH overtone confirmed the formation of protonated silica in the reaction product. The montmorillonite structure was partly disrupted after 2 h and significantly after 4 h treatment. The spectrum of SAz-8h corresponded to protonated silica. The adsorption of pyridine on acid-treated samples modified the first OH overtone (2n$_{OH}$) region. While the position of the 2n$_{OH}$ band remained nearly unchanged the 2n$_{SiOH}$ band almost completely disappeared. Silanol groups as a weak Brőnsted acid sites formed H-bonds with pyridine-nitrogen. As a result the SiOH overtone was shifted to lower wavenumbers and overlapped with broad complex band near 7100 cm^{-1}. After pyridine adsorption the CH overtone band (2n$_{CH}$) corresponding to physisorbed and/or H-bonded pyridine appeared near 6000 cm^{-1} in the spectrum of Na-SAz. The shape and position of the band was only slightly changed if pyridine was adsorbed on acid-treated samples. Upon heating the H-bonded pyridine molecules were released as confirmed the reappearance of the 7315 cm^{-1} band and decreased intensity of the 2n$_{CH}$ overtone. Almost complete loss of pyridine band was observed for Na-SAz and amorphous silica heated above 170 ºC, while well-resolved 2n$_{CH}$ band was still present in the spectra of 2 and 4 hours treated samples. Its position, however, was considerably shifted to the higher wavenumbers. Partly leached acid-montmorillonite provided protons for generation of pyridinium cations. Thus the bands at 6096 and 6065 cm^{-1} in the spectrum of SAz-2h heated at 230 °C were assigned to C-H vibrations of pyridinium cations.The obtained results showed that NIR spectroscopy candistinguish different pyridine species onmontmorillonite surface.

Hydration kinetics of smectites in comparison to vermiculite and illite

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Natural phyllosilicates and especially swellable phyllosilicates are characterized by an intrinsic structural heterogeneity of the silicate layers [Wolters, et al., 2009] and interlayer occupation. These heterogeneities within the material lead to coexistence of different hydration states. Different hydration states cause inconsistency in calibration in-situ methods for water content measurements based on permittivity measurements. Thus, understanding of hydration of smectites is mandatory for understanding and controlling related processes and for monitoring of the hydration state in various applications. The hydration properties and the resulting interlayer organization of water (0W, 1W, 2W) were thoroughly studied for interlayer cations in particular by Ferrage et al., 2005; 2007 (and references herein). However, correlation with structure properties was restricted for few samples, although water content correlates more strongly with the exchangeable cations (measured as cation exchange capacity - CEC) than with layer charge [Kaufhold, 2006] and the ratio of interlayer to edge exchangeable cations is a fundamental parameter for hydration. This correlation is even more pronounced for small particles with an increased contribution from edge sites to CEC [Emmerich et al., 2011].

Different purified and homoionic (Na^+) smectites (<0.2 µm) of different layer charge and charge location (octahedral vs. tetrahedral charge), a vermiculite and a very fine grained illite were selected. The aim of the present work is to study the kinetics of adsorption and desorption of water on homoionic smectites and vermiculite compare to a non-swellable illite.

First results from water vapor adsorption isotherms show different kinetics of smectite hydration at low and high relative humidity (r. h.) with respect to equilibration time. In addition the illite sample seems to have the same hydration dynamics at <30% r.h, which indicates that water adsorbs only on the external surfaces and the edges at low relative water vapor pressure.

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Adsorption of amino acids on ground montmorillonite

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Mechanical grinding of clay minerals is an important process occurring in industry and nature. In nature, abrasion of minerals is one of the principal weathering processes, recognized mainly in dry regions. It causes substantial changes of their structure, crystallinity, and properties [1]. The main observed changes were the breakage of large aggregates, the reduction in the thickness of tactoids by delamination, the increase of surface area, and the formation of colloidal matter. It has been shown that grinding shortens the time necessary for the further reaction.

These minerals could play an important role in the origin of life on earth, because they participate in the adsorption of biomolecules on their surface from dilute solutions [2]. Immobilization of amino acids on clays is a suitable way for the preparation of organoclays which have applications as pollutant adsorbents, rheological control agents, paints, and cosmetics.

The aim of this work is to describe the influence of dry grinding in a high-energy planetary ball mill on the adsorption properties of Na-montmorillonite. Samples of Na-Kop were ground for 2, 4 and 6 minutes and compared with an untreated sample. These samples were used as adsorbents of two amino acids, l-cysteine and l-glutamic acid, from aqueous solutions. IR spectroscopy, X-ray diffraction analysis, thermal analysis and the determination of C and S contents were used for their characterization.

Amorphization of the montmorillonite caused by intense grinding occurred. The grinding process affected the structure and chemical bonds in the Si-O-Si, Si-O-Al, and O-H groups of the mineral. Most of the absorption bands were undetectable in the IR spectrum of the sample ground for 6 min which adsorbed the highest amounts of the amino acids.

The authors acknowledge the financial support of the Grant Agency APVV (grant APVV-0362-10).

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Investigation of the kaolinite inner-OH and outer surface-OH with new molecular cluster model using quantum chemical methods

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Kaolinite is a remarkable industrial raw material. In addition to empirical approaches, theoretical modeling can also provide significant insights about clay minerals. Despite its periodic structure, molecular cluster models can also be used to investigate their reactivity and structural properties.

As first step, we developed a molecular cluster model following the rules of coordination chemistry. We used this model to describe realistically a 1 nm moiety of the kaolinite. It includes both the octahedral and tetrahedral layers of Al^{3+} and Si^{4+} ions connected by their direct chemical environment.

In this model, the internal HO^- groups and adjacent Al^{3+} ions have a chemically complete environment. Thus, these can be used as indicators for gauging the level of theory dependence of the optimized structural results. We evaluated the performance of a representative set of functionals, basis sets, and identified pitfalls and caveats. The outer surface HO^- groups are equally important in the clay minerals. Therefore we performed similar test as for the inner HO^- groups. On the basis of these tests we selected the most appropriate quantum chemical method, which can describe the structure of clay minerals most realistically, as well as adsorption and intercalation mechanism.

Hydration properties and interlayer structure of di- and tetraoctylammonium-montmorillonite

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Modification of montmorillonites with cationic surfactants is widely used method to prepare inorganic/organic hybrid materials with properties suitable for different applications. Understanding microstructure and hydration potential of organo-montmorillonites is of high importance in clarifying their adsorption characteristics towards different organic compounds. The objective of the present work was to examine the effect of loading amount of di- (2C8) and tetraoctylammonium (4C8) cations on the arrangement of surfactant within montmorillonite interlayers and on the hydration properties of organo-montmorillonites. The montmorillonite JP (Jelšový Potok, Slovakia) and 2C8- and 4C8-salts in loading concentration range 0.2 - 2.0 mmol.g^{-1} (corresponding to 20 - 200% of the CEC of JP) were used for organoclays preparation. Carbon analysis, XRD, and IR spectroscopy were used for the samples characterization. The highest carbon content of 172% and 196% of CEC was determined for 2C8 and 4C8, respectively, at 2.0 mmol.g^{-1} of the cation used for preparation. The d_{001} value of 2C8- and 4C8-JP showed creation of monolayers, bilayers and paraffin arrangement in dependence on the number of alkyl chains and loading amount. The bands of CH_2 stretching and the first overtones were used to probe the ordering of the intercalated cations. With growing amount of surfactant the bands were shifted from the positions characteristic for disordered *gauche* conformers to lower wavenumbers indicating increasing number of *all-trans* conformers. The hydration properties of samples were investigated by gravimetry and NIR spectroscopy using H_2O combination band near 5250 cm^{-1}. Difference in the area of this band at 52% and 0% relative humidity reflected the quantity of adsorbed water. Both methods demonstrated the evident effect of the amount of adsorbed or intercalated cations and number of alkyl chains on the hydration of montmorillonite. The water content decreased with growing quantity of surfactants and alkyl chains. Almost linear decrease of water content from 8.1 to 1.8 mass % and from 7.0 to 1.0 mass % was observed for 2C8 and 4C8 cations, respectively with increasing loading cation content from 0.2 to 1.0 mmol.g^{-1}. Further increase of cation content reduced the amount of water only negligible.

Application of inverse gas chromatography for the characterization of clay mineral surfaces

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The surface characterization of clay minerals is of high importance in the light of their application as fillers, composites or hybrid materials. Surface properties can especially influence the chemical and mechanical characteristics of nanohybrid materials and clay -polymer composites. The standard nitrogen-adsorption experiments provide useful information on the specific surface area, the pore size and pore volume distribution. Surface adsorption of different test materials (e.g. CO_2, NH_3, pyridine) provides information on the acid-base properties of the surface. At the same time, no general techniques are available for the characterization of the surface energy.

In this work the method used for the characterization of chromatographic stationary phases was applied for the determination of the surface energy and the acid-base properties of

kaolinites and delaminated kaolinites of varying structural order. The kaolinites were used as stationary phases. A test mixture made of chloroform, dichloromethane, nitromethane, ethyl-acetate, acetone and acetonitrile was injected at 90 °C under isothermal conditions using a He carrier gas and TCD detector. The dispersion component of the surface energy, the specific free energy of adsorption and the acid-base constants were calculated from retention data using the Dorris- Gray, the Papirer and the Gutmann method, respectively.

As a result of delamination, the surface energy increased by 17-82%, depending on the structural order. The specific free energy of adsorption increased 1.3-2 times showing a strong correlation with the morphology of the mineral. The change in surface acidity/basicity is also significant. For pseudo-hexagonal systems the basic, while for the tubular ones the acidic character predominates.

This work was supported by the European Union in the frame of the TÁMOP-4.2.2/A-11/1/KONV-2012-0071 and TÁMOP 4.2.4. A/2-11-1-2012-0001 projects.

Water soluble ions in non-marine bentonites (Bavaria, Germany)

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Bentonites in Bavaria, Southern Germany, formed in a distinct freshwater environment and often show reduced (blue, green, grey) and oxidized (yellow) facies. Soluble ions in bentonite may provide new insight into the geologic history of the clays and the composition of involved fluids assuming that water soluble ions are residues of ancient fluids. This study relates electrical conductivity (EC), pH and soluble ion concentrations in bentonites to a geological context. Profiles were sampled in three bentonite deposits with different oxidation facies and geological environments. Bentonites were prepared as 2% suspensions with de-mineralized water to extract water soluble ions and exchangeable cations and allowed to equilibrate for 5 days. Preliminary results from one deposit show that yellow oxidized bentonites have a greater variability of EC (20 to 64 µS/cm) and lower pH (7.7 to 8.7) than bluish reduced bentonites with EC (44 to 71 µS/cm) and pH (8.9 to 9.4). A strong positive correlation of pH with EC is noted in oxidized bentonites, while pH of reduced bentonites is unrelated to EC. The preliminary results indicate that blue bentonites are relatively homogeneous with respect to EC and pH, while the greater variability of soluble ions in yellow bentonite relate to late oxidation processes probably involving sulfides.

Interaction of selected organic molecules with immobilized Cu^{2+} cations in montmorillonite

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Fixation of small cations such as Li^+ in montmorillonites has been used for layer charge modification. Although Li^+ and Cu^{2+} ions are of similar ionic radii, the process of Cu^{2+} fixation is more difficult. The objective of this work was to determine the location of Cu^{2+} in heated montmorillonite using electron spin resonance spectroscopy (ESR). The extent of immobilization of Cu^{2+} was determined by solvation ability of the materials. Samples with different position of Cu^{2+} in the interlayers and its immobilized portion were prepared by heating the Cu-montmorillonite from Jelšový Potok (CuJP) for 24 hours over a temperature range between 100 and 400 °C. Fixation caused the decrease of cation exchange capacity. Dimethyl sulfoxide (DMSO) and acetonitrile (AN) were utilized to depict the solvation ability of heated CuJP samples. The amount of adsorbed solvent was determined by gravimetric analysis and compared with the changes in the interlayer distance. The Cu^{2+} complexes in the interlayer space showed a weakly rhombic distortion and distinctive hyperfine coupling constants were not observed in the ESR spectra of the samples heated above 150 °C. The broadening of spectral lines as well as the loss of hyperfine structure was mainly caused by the dipole-dipole interactions between the two closest Cu^{2+} ions. Solvation by AN shows small changes in ESR spectra for sample heated at 200 °C, due to the interaction of AN molecules with immobilized Cu^{2+}. Solvation of samples heated above 200 °C induced just negligible changes of ESR spectra. Solvation by DMSO caused contraction spectral lines and decreased anisotropy for all heated samples. DMSO can interact with Cu^{2+} deeply in the ditrigonal cavities of montmorillonite layers, therefore immobilization of Cu^{2+} by heating up to 400 °C was partially reversible.

The authors acknowledge financial support of the Slovak Research and Development Agency (APVV-0362-10)

Pillared montmorillonites as catalysts for removal of chlorinated volatile organic compounds from air – textural characterization

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Pillaring of natural montomorillonite with appropriate polycations is one of the most promising possibilities to obtain specific catalysts for different reactions including removal of chlorinated volatile from exhaust gases. Their catalytic properties depend both on the type of introduced polycations and the texture (specific surface area, pore volume and pore volume distribution) which is developed during pillaring in contrast to classical catalyst. In the latter case active material is deposited on the appropriate support with high surface area and porosity. Thus independly of the introduced polycation the resulting texture of the final material will depend on the preparation method i.e. removal of chlorides from starting material (Na-mt) by repeated washing or dialysis and drying method of pillared montmorillonites: freeze drying and evaporation or drying in an oven.
The textural properties of potential catalysts for removal of chlorinated volatile organic compounds (CVOCs) based on Na-montmorillonite (Na-mt) i.e. Ti-PILC, Zr-PILC and [Ti,Zr]-PILC, pillared derivatives before and after doping with Pd, Cr and (Pd,Cr) (1% wt.) were determined. It was noticed that the preparation of starting Na-mt in particular the method of chlorides removal influenced its textural properties. Na-mt washed by dialysis (Na-mt-dial), after drying had almost 3 times higher surface area then purified by centrifugation (Na-mt-cen), half of which was associated with micropores, which practically was not in Na-mt-cen. Micropores mainly influenced the textural properties of pillared montmorillonites. Their surface area constituted about 80% of total surface area and was highest for the [Ti,Zr]-PILC sample. Simultaneous pillaring with titanium and zirconium polycations led to formation of a material with hybrid textural properties which fall between the properties of Ti-PILC and Zr-PILC. The effect of doping with Pd, Cr and (Pd,Cr) on the pillared montmorillonites texture was practically unnoticeable, only for Cr-Zr-PILC more visible, suggesting that part of micropores were blocked.

The work was partially financed by the UST Academy of Mining and Metallurgy the research project no 11.11.140.319.

Different tools for the investigation of micro fabric and damage patterns in claystones (Opalinus Clay, Mont Terri)

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Claystones are potential host rocks for high-level radioactive waste disposal. They are very complex in composition and micro fabric as well as their thermo-hydro-mechanical (THM) behaviour. Until now, the processes are not sufficiently understood. Previous studies (e.g. Kaufhold et al. 2013) showed that the micro fabric has a significant influence on THM properties.

This study presents different tools to investigate the micro fabric and damage patterns of claystones before and after the mechanical loading in a triaxial cell. These methods also considered different scales as well as different mineral composition.

KAUFHOLD, A., GRÄSLE, W., PLISCHKE, I., DOHRMANN, R. SIEGESMUND, S. (2013). Influence of carbonate content and micro fabrics on the failure strength of the sandy facies of the Opalinus Clay from Mont Terri (Underground Rock Laboratory). Eng. Geology, 156, 111-118.

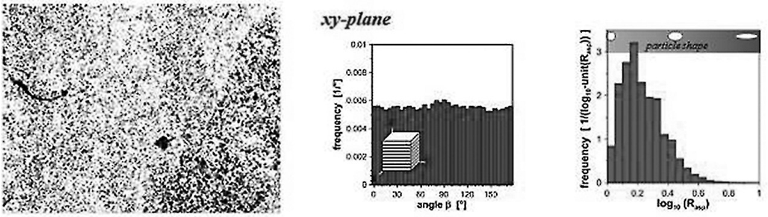

Figure 1. Micro fabric investigation by using BSE images (1) extracted carbonate particles, (2) particle orientation, and (3) particle shape

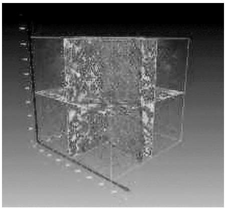

Figure 2. CT-image showing the pore system and the damage pattern

Characterization of functionalized PCH composites derived from Laponite

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A functionalized porous clay heterostructures (PCH) have been prepared through the surfactant directed assembly of organosilica in the galleries of laponite. The reaction involved hydrolysis and condensation of tetraethoxysilane in the presence of intragallery surfactant templates. Resulting pure silica composite support was functionalized by a post-synthesis impregnation with tin chloride pentahydrate to obtain Si/Sn = 10. The objective of this study was to investigate the tetravalent (Sn^{4+}) cations distribution in the silica structure of PCH composite derived from the synthetic layered mineral Laponite. Elemental analysis revealed incorporation of tin into silica structure. High quality pores and the high specific surface area were still present after impregnation of PCH.

FTIR spectroscopy obtained in the MIR region indicates the localization of the tin in the PCH silica network. The decrease of maxima bands intensities at 1093 cm^{-1} and 805 cm^{-1} corresponding to the antisymmetric and symmetric Si-O stretching vibrations, respectively, upon Sn doping indicates a relative decrease of the amorphous silica content. The Si-O stretching vibration at 1028 cm^{-1} and Si-O-Si bending mode around 466 cm^{-1} of the Laponite tetrahedral sheet were not affected after impregnation.

According to results obtained in the NIR region impregnation of PCH with tin reduces the intensity of SiOH, Mg_3OH and $LiMg_2OH$ groups of Laponite on the surface. Thermal treatment causes breaking of the Si-O-Si linkage, Sn incorporation into TEOS-derived silica network and creation of new terminal Si-OH bands at the surface. This effect confirms that tin atoms can be incorporated into the network of amorphous silica developed during PCH synthesis despite of the difference in size of Sn^{4+} (0.55 Å) and Si^{4+} (0.26 Å) cations. The ^{119}Sn Mössbauer spectroscopy revealed two components in the Sn-PCH sample. About 30% corresponds to the Sn atoms incorporated into silica structure, whereas the rest have parameters characteristic for SnO_2. This indicates that impregnation of PCH structure by tin atoms leaves some extra lattice tin species as a distinct phase.

This work has received funding from the Polish-Norwegian RP operated by the National Centre for R&D under the Norwegian Financial Mechanism 2009-2014 PC No Pol-Nor/210445/53/2013.

Synchrotron X-ray Scattering and Monte Carlo Simulations of Structure and Forces in Silicate Nanoplatelet Dispersions

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Clays are the world's most widely used natural material, however, little is known regarding the microstructure as well as the forces involved in clay-water interactions, and their influence on the swelling properties. The utilization of clay platelets is nowadays a key in a number of biological and industrial applications e.g. nuclear waste management. Bentonites from different natural sources and pure Na/Ca montmorillonite platelets have been studied experimentally and theoretically. Small angle X-ray scattering (SAXS), dynamic light scattering (DLS), nuclear magnetic resonance (NMR), X-ray absorption spectroscopy (XAS), transmission electron microscopy (TEM) and Cryogenic-TEM were applied to provide direct information about the structure of dry clays as well as clay platelets in equilibrium with a bulk solution of given ionic composition, temperature and pH. Monte Carlo (MC) simulations have been used to predict the osmotic pressure of montmorillonite dispersions. The swelling behavior is mainly regulated by counterion valency and surface charge density. Divalent counterions and high surface charge density lead to a limited swelling, while monovalent counterions favor a large swelling. This study has also investigated the aggregation of nanoplatelets in clay-water systems, in order to understand the effect of platelet size on the structure and swelling behavior. A new twist on aggregation phenomenon is that, really small platelets (~ 20 nm) do not form a tactoid, whereas larger platelets give rise to larger tactoids. The platelet size controls the aggregation and microstructure of silicate platelets into tactoids following an empirical relation as: $N \simeq \delta + \alpha D_{eff}$, where N is the number of platelets per tactoid, D_{eff} is the effective diameter of platelets, δ and α are constants.

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Clay minerals in diagenetic and low temperature metamorphic environments

Illite+smectite as components of shales

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Illite+smectite accounts for 30-50 wt.% of shale mineral composition and for ca. 1/3 of the mass of all sedimentary rocks. Both due to its large quantity and unique characteristics illite+smectite control numerous properties of the bulk shale.

Smectite is a low-temperature mineral: the product of weathering and low-temperature diagenesis. In shales it can be then both detrital and authigenic. In surface temperatures and close to neutral pH it is very stable, as evidenced by the finding of pure dioctahedral smectite in the Ediacaran (>542 Ma) mudstones of Podolia. Illite may also form at surface temperatures in rare environments of elevated pH (>9), but it is the dominant product of typical silicate rock alteration at elevated temperatures. Illite survives temperatures up to 300 ^{o}C, when it recrystallizes into coarse-grained mica, and is also quite resistant to weathering. Thus in shales, illite - like smectite - can be, and most often is, both detrital and authigenic. If the substrate of illitization is smectite, mixed-layer illite-smectite minerals appear, and their composition evolves gradually towards end-member illite with increasing temperature (the thickness of illite fundamental particles increases). This process terminates when the maximum paleotemperatures are reached. An admixture of illite-smectite is present in almost every shale sample, and the layer ratio can be quantified by XRD, offering the most universal proxy for the maximum paleotemperatures.

All clay mineral crystals are plates, with high aspect ratios. Smectite and thin illite crystals are not rigid but flexible and they have electric charge on the surfaces, which makes them form quasi-parallel aggregates. This property creates microporosity and anisothropy of the shale fabric, the properties evolving with the increasing overburden and with the illite crystal growth.

Smectite crystals and smectitic interlayers in illite-smectite crystals are the only components of common shales with large surfaces (up to ca. 800 m^2/g), which are charged, thus capable of exchanging cations (CEC), adsorbing water, and organic molecules. Thus illite+smectite control electric properties of shales (their CEC) and shale behavior on contact with fluids.

A great majority of shale boron is contained in illite layers. This property offers an opportunity of quantifying the illite+smectite component of shales via neutron absorption measurements of borehole geophysics (S_a).

In common shales a few to more than 50% of potassium in illite is substituted by ammonium. The level of substitution is controlled by the supply of ammonium. Shales import ammonium from the outside, as they can fix more than available locally from the diagenesis of organic matter. The ammonium fixation in shale illite is the key process of the global nitrogen cycle.

Authigenic illite is the only common K-bearing diagenetic product, thus containing information about the age of the maximum paleotemperatures (K-Ar dating).

20 years of the Crystallinity Index Standard – a progress report

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The Crystallinity Index Standard (CIS) developed by Warr & Rice (1994: *Journal of Metamorphic Geology*) is a calibration approach used to standardized the Full-width-at-half-peak-maximum (FWHM) parameter of the X-ray diffraction basal reflections of clay minerals so that different laboratories can more easily produce the same results from the same rocks. The most common use of the CIS standards has been to calibrate the FWHM of the illitic 10 Å and the 14 Å chlorite reflections, referred to as the Kübler and Arkai index, respectively. These indexes are widely used for determining the grade of diagenesis and low temperature metamorphism of argillaceous rocks, allowing recognition of diagenetic, low anchi-, upper anchi- and epi-zone conditions. The use of these rock chip standards that require sample preparation has generally taken over the use of polished rock slabs as they have the advantage of calibrating all the differences between laboratories, and not just variations caused by different X-ray diffraction machine settings. One often stated "problem" with the Crystallinity Index Standard is that the FWHM values used are significantly broader than B. Küblers' original scale of the Neuchatel Laboratory: which is actually the case. The reason for this difference is that the CIS scale made an attempt to reproduce Küblers' original "anchizonal" values indirectly using the polished rock standards circulated by H. Kisch. The procedure failed to work because the sample preparation differences between the laboratories in question were not included. Despite the relevant broadness of the CIS scale, this standardization procedure has found widespread usage over the last 20 years and has achieved its goal in enabling researchers to produce directly comparable results between laboratories. This presentation will make some suggestions for the future of the CIS procedure, which can be openly discussed in the accompanying "Round table to discuss problems in "Kübler index" standardisation".

Standardisation, calibration and correlation of the Kübler-Index

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A multiple inter-laboratory Kübler-Index (KI) calibration with illite Kübler-Frey-Kisch (KFK) standards is presented and compared with KI values calibrated with CIS standards as used in the last two decades in very low-grade metamorphic studies. Comparing both data sets the CIS values show a higher full width at half-high maximum peak intensity. In all cases due to broadening effects on the CIS KI, a shift of zone-limits, specifically the diagenetic zone/anchizone boundary, is produced in geographical dimensions in a metamorphic map-view. A comparison with coal indices and index minerals will demonstrate some discrepancies between the CIS values and KFK calibrated KI shown in a pressure-temperature diagram with the subdivisions of diagenesis and sub-blueschist and sub-greenschist facies.

Combining standardised KI and vitrinite reflectance (VR) measurements a coherent data set for compilation studies can be generated from the data of different research groups. This attempt to establish a unified database of independent measures to determine diagenetic/metamorphic zones with different analytical instrumental methods are indispensable to present metamorphic maps at very low-grade conditions. Given that the KFK standards are difficult to preserve for the future and presumably they will be replaced with ongoing time by the CIS standards, a rescue of the laboratory settings from Frey, Kübler and others is done. After having compiled the KI - VR zones for the “New Metamorphic Map of the Alps”, the presented calibration and inter-laboratory correlation gives a chance to save the KI values obtained by very different preparation procedures applied. This is an important step for further studies in an area like the Central Alps with a very high data grid. Using the same calibration and preparation technique no fundamental problem in data comparison is achieved for VR data operation. The main problem arises when rock maturity is compared with CIS calibrated KI values. KI values obtained by the CIS calibration are not compatible with KFK calibrated KI. Nevertheless, it is evident that a uniform use of CIS and KFK-KI standardisation procedure is needed to avoid confusions and different scales for determining diagenetic grade and incipient metamorphic grade.

Low-grade metamorphic study based on Árkai Index and Kübler Index correlation in basins of Southern Vosges (NE France)

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Low-grade metamorphic studies involving clay mineral alteration and reaction progress are able to help in deciphering the thermal evolution of sedimentary basins. Sheet silicates like illite and chlorite are very common in basinal sedimentary sequences. Therefore, they are used in a wide variety of method applied for determining the grade of diagenesis and low-temperature metamorphism: the Kübler Index (KI) and the Árkai Index (AI), respectively. Although the ÁI method is considered to be slightly less sensitive than the KI method, a reliable correlation between both methods exists in some metamorphic domains where a simple heat-flow history and minimum tectonic deformation occurs.

Our investigated basins are located in Southern Vosges, and characterized by different units (Markstein and Oderen) composed of deep marine turbidites (Upper Devonian to Upper Visean, Krecher (2005)).Our study focuses on the Markstein basin, which is surrounded by granitic intrusions emplaced at ca. 340 and 326 Ma. The previous study of Petrini & Burg (1998) showed a deformation characterized by regional folding. Preliminary results of this study indicate anchizonal to epizonal metamorphic conditions using the KI method, whereas ÁI values are slightly higher in grade indicating more epizonal conditions. No obvious correlation between KI and ÁI values is observed. However, different groups of samples can be recognized based on their mineral paragenesis and their location in the basin. In these different groups, a reliable correlation between KI and ÁI values is present. Evolution of KI and ÁI seems to be here highly controlled by lithology. The K white mica *b* cell dimension in the Markstein basin characterizes an intermediate facies series with values around 9.00 to 9.02 Å.

A complementary study is also being performed in the southern part of the Giromagny basin for comparison.

Krecher (2005), PhD thesis Freiburg I Br..
Petrini & Burg (1998) Geol France, 2**.**

Differences of maturation between clays and organic matter in materials altered by the Monchique pluton (South Portugal)

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This contribution explores the clay behaviour in the surrounding of a pluton to infer aspects related to thermal evolution in the absence of reaction driving-forces other than temperature. During the Cretaceous, the Monchique pluton was emplaced in metapelite and greywacke host rocks affected by previous very-low grade metamorphic conditions in the South Portuguese Zone of the Iberian Variscan chain. The intrusion produced a thermal aureole with hornfels in the contact, containing cordierite, andalusite and biotite. Apparently, thermal effects persisted for more than 3 km from this syenitic igneous body, as evidenced by vitrinite reflectance values higher than 4% and natural coke with mosaic optical texture. Nevertheless, the host rocks close to the contact that were not transformed to hornfels show the same textural, chemical, mineralogical and crystal-chemical characteristics as the equivalent clastic rocks from the distant rocks of Brejeira and Mira Formations. Quartz and white K-mica are the main phases in all the samples. Illite is the predominant constituent of the <2 µm fraction and significant amounts of kaolinite, intermediate Na-K mica and chlorite were also detected in samples from the different cross-sections. The irregular distribution of the illite “crystallinity” (KI) values indicates diagenetic-low anchizone conditions and locally high anchizone, in concordance with previous studies of these flysch sequences (Abad et al., 2001, 2002) and crystallite thicknesses of micas measured on lattice-fringe images gave values in the range to those of the metapelites far from the pluton with an average of 850 Å. This difference between the reaction progress of inorganic and organic materials is interpreted to be related to the slow reaction rates of the clay minerals. In addition, the absence of pervasive tectonic effects during the thermal event of the pluton emplacement is a factor that could have deprived the clay minerals of one of the main driving forces for their reaction progress. Future studies of zircon in the greywackes opens the possibility to clarify the real temperature reached by the rocks and the timing of the thermal events, as their fission tracks anneal around 200 ºC.

Abad I, Mata P, Nieto F, Velilla N (2001) Can Mineral, 39: 1571-1589.
Abad I, Nieto F, Velilla N (2002) Schweiz Mineral Petrogr Mitt, 82: 303-324.

Diagenesis and metamorphism of the Meso-Neoproterozoic and the Lower Paleozoic along profile Yueyang-Linxiang in northeastern Hunan province, China

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The Meso-Neoproterozoic and the Lower Paleozoic along profile Yueyang-Linxiang in northeastern Hunan Province, China underwent diagenesis and epimetamorphism. Illite crystallinity Kübler index (in crystallinity index standards (CIS) scale) of the <2 mm fractions ranges from 0.23 to 0.49°∆2 q while chlorite crystallinity Arkai index ranges from 0.24 to 1.50°∆2 q. This declares that the samples of the Meso-Neoproterozoic and the Lower Paleozoic along the profile show a diagenetic and epimetamorphic overprint. The peak metamorphic temperature is determined with the IV site chlorite geothermometer at 360 °C. This result partly agrees with the conclusion of the lower greenschist and greenschist facies of the Banxi (1000-800 Ma) and Lengjiaxi (1850-1000 Ma) Groups. However, it is not in agreement with grade of the sedimentary cover of the Lower Paleozoic. The b_0 cell dimension values of illites (K-mica) range from 0.900 to 0.905 nm and, on average, as 0.903 (nm) for the Meso-Neoproterozoic. Based on cumulative frequency curves of illite (K-mica) b_0 cell dimension, the peak metamorphic pressure of the Meso-Neoproterozoic along the profile was derived of the intermediate pressure type. Most illites occur as $2M_1$ polytype and some of them in the Neoproterozoic as a mixture of $2M_1$+1M types.

The low grade to very low grade metamorphism overprinting the Proterozoic and the lower Paleozoic implies that the so called “Jiangnan ancient land or Jiangnan orogeny [1]” cannot be related with the “Grenvillian orogenic event (continent-continent collision occurred about 1190-980 Ma with high grade metamorphism e.g. granulite facies [2])”; instead, it might be a continuous amalgamation product between the Yangtze and Cathaysia blocks.

[1] Ren Jishun, On the geotectonics of southern China. Acta Geologica Sinica, 1990, 64(4), 275-288

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New insights in the definition of phyllosilicate stacks in diagenetic-metamorphic environments – examples from clastic to metaclastic rocks in Turkey

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The origin and diagenetic/metamorphic grade determination via mineral chemistry of phyllosilicates were investigated in Paleozoic-Lower Mesozoic clastic-metaclastic rocks from different tectonic units of Turkey. Energy Dispersive Spectroscopy and Electron Microprobe analyses were performed on the phyllosilicates (illite/muscovite, paragonite, NaK mica, chlorite, mixed-layers (illite (I)-smectite (S), Chlorite (C)-S, I-C) from chlorite-mica stacks (CMS)-bearing samples. The optical microscopic and back scattered-electron images of polished carbon-coated rock sections show that the orientations of matrix and CMS are different for extensional and collisional basins. Paragonite, NaK mica, pyrophyllite and dickite, which are index and/or distinctive minerals for extensional basins, were observed as 1-20 mm thick bands and/or layers within the CMS and thus of detrital origin rather than authigenical formed in the matrix. Chlorites in the CMS display compositions of brunsvigite and diabantite in diagenetic samples, mostly ripidolite and partly brunsvigite in anchimetamorphic samples, and thuringite and chamosite in epimetamorphic samples. From diagenesis to epimetamorphism, Al^{IV} and Fe+Mg increases, whereas Al^{VI} decreases. Chlorites from extensional basins have high Fe (Fe*=Fe/Fe+Mg) content (>0.5), while from collisional basins have higher Mg content (Fe* <0.6), indicating felsic and basic origins, respectively. Chlorites with the highest Fe amount were determined in samples from extensional basins associated with paragonite, NaK mica, pyrophyllite and dickite; however chlorite with the highest Mg amount containing also Mn and Cr were detected in samples from collisional basins. Muscovites exhibit compositional differences that are characterized by decreasing Si and increasing Na+K values from diagenesis to epimetamorphism. The types of white micas range from paragonite to NaK mica and muscovite for extensional basins and from muscovite to phengite for collisional basins. Mineral chemistry investigations testify that chlorite compared with the mica chemistry is a more decisive parameter depending from origin, diagenetic/metamorphic grade and the geodynamic setting. Because of the presence of pyrophyllite and dickite bands or layers within the stacks, the use of phyllosilicate stacks (PSS) term instead of CMS would be more appropriate.

Chlorite crystallizations induced by fluid circulation and deformation along a thrust fault zone (Pic de Port Vieux thrust, Pyrenees)

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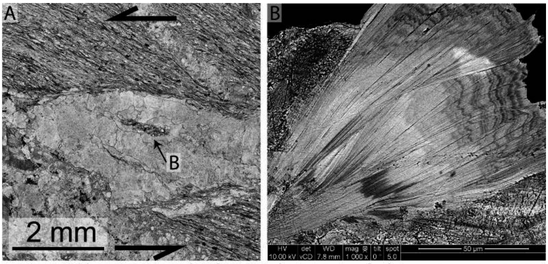
The Pic de Port Vieux thrust, a second-order thrust related to Gavarnie thrust in the Axial Zone of the Pyrenees, juxtaposes Triassic pelite in the hanging-wall and Cretaceous limestone in the footwall. In order to investigate the mineralogical and geochemical changes induced by deformation and subsequent fluid flow, sampling of host rock was conducted along a complete transect from both rocks and also on synkinematic quartz-chlorite veins (Fig. A).

Mineralogical characterization combined optical microscope, cathodo-luminescence and Scanning Electron microscopic images, bulk chemical XRF and XRD analyses, microprobe and X-ray mapping, as well as Raman, Mössbauer and µXanes spectroscopies. Several geothermobarometers were used to determine the PT conditions.

The data suggest the circulation of a 300 °C reductive fluid along the thrust fault and its interaction with the host rock. Newly formed synkinematic chlorites precipitate along shear and extension veins. Locally, in extension veins, unusual oscillatory Fe-Mg zoned chlorites are also present (Fig. B). The origin of these chemical zonings and their significance in this low metamorphic context will be discussed.



A. Quartz-chlorite vein in pelite from Pic de Port Vieux fault zone, Pyrenees, Spain
B. Zoom on oscillatory zoning pattern chlorite.

Dewatering path-ways evidenced by clay minerals in a diagenetic/very low-grade tectono-metamorphic mélange (Arosa zone, Eastern Switzerland)

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Different tectonic elements of the Arosa zone mélange show a distinctively different metamorphic history. Diachronous, poly-metamorphic and differences in the grade of Alpine metamorphism are detected. This is evidenced by the wealth of Kübler Index (KI) - vitrinite reflectance (VR) measurements and kinetic numerical modeling, bituminite reflectance, illitization indices (related to the smectite-illite reaction progress), K-white mica b-cell dimension determinations, index minerals and microprobe data.

The matrix sediments of the Arosa zone mélange are overprinted by a high-grade diagenesis to high anchizonal metamorphism. In contrast, Lower Austroalpine fragments in the mélange and the adjacent Austroalpine tectonic units were overprinted by a widespread syn-sedimentary burial and/or an orogenic epizonal metamorphism. Completely different in grade, the flysch units of the mélange zone are of lower diagenetic thermal character.

Depicting a partly tectonic dismembered mosaic-like thermal pattern, in the Arosa zone some other anomalies were found. These were detected by comparing the KI-VR, KI-Sm% (smectite content in illite) and VR-Sm% relations together with the occurrences of vermiculite and low ordered illite or kaolinite. The anomalies contrast with the mapped zones of high diagenesis to epizone grade.

In general, a smectite content trend from 15% in the north to 0% in the south is recognized and fits with a strongly smoothed metamorphic data grid. But at thrusts, mélange sheer zones and broken formations, the smectite content increases frequently to 10 to 20% and disordered clay minerals are common. Also the KI values are anomalously broad, indicating lower grade than the metamorphic pattern. Shale with broad KI values shows a change to green colors coupled with the occurrence of vermiculite-chlorite-smectite phases. KI values based on decomposed reflections are irregular but show a slight increasing trend of aggradation to the south.

Together with better-ordered clay minerals a cooked bituminite precipitated with the clay minerals indicating hot fluid migrations. The Sm anomalies build a net-like structure and can be related to thrusting and interpreted as forming syn-to-late mélange formation. The overall structure indicates dewatering pathways from dehydration reactions active during peak metamorphism and which overprinted the orogenic regional thermal pattern.

Illitization of Ordovician bentonites in the Baltic Basin – Where all this K was taken from?

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The illitization of smectite in K-bentonites is mainly controlled by the temperature and availability of potassium. Identification of such K sources is quite often problematic. The Ordovician sedimentary succession of the Baltic Basin contains numerous K-bentonites. Those beds are found within carbonate successions in stratigraphic intervals where they form distinct series composed of numbers of rapidly alternating beds. Shallowly buried and uncompacted sediments in the Baltic Basin are thermally immature (CAI, TAI ≤1) but mixed-layer minerals are significantly illitized (<20% of expandable layers). Mass-balance calculations show that for illitization of these bentonites an additional K flux is needed in the N and NW parts of the Basin. This was explained in literature with a prolonged flush of K-rich fluids in relation with the latest tectonic phase of the Scandinavian Caledonides. If the potassium was derived from regional scale fluids, then the alteration and the rock-fluid interaction should be seen at a wider scale. The bentonite bearing carbonate-rock sections were studied using mineralogical (XRD), textural (SEM) and geochemical (ICP-MS) analyses in order to characterize K distribution and occurrence in bentonite host rocks. Mass-balance mixing modelling shows that the volcanic component in sections with bentonite beds reaches up to 50-60% in the host rock. This indicates that volcanic material is not only located in discrete bentonite beds representing single events or series of subsequent eruptions. Also a significant amount of volcanic tephra was dispersed or re-deposited into the carbonate host rock while there is no evidence for a regional scale K-rich fluid intrusion in sedimentary sequence surrounding the bentonite interval. Instead, we suggest that K was derived from the dissolution of dispersed volcanic material and the mobilized K was preferentially taken up by the authigenic smectite and K-feldspar nucleating during devitrification of the volcanic glass in bentonite beds.

The role of deep-water glauconitization in the sedimentary iron cycle

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The iron bioavailability significantly influences biological processes in modern (deep sea) ecosystems and in particular in superficial marine sediments, and has been of major significance throughout the geological record. Reservoir-flux models are currently used to examine mass balance relationships in the marine iron cycle, assuming steady-state between continental iron sources and marine sulfidic sediment sinks. However, the characterization and quantification of iron uptake by glauconitization has not been included and therefore its importance in the marine sedimentary iron cycle remains uncertain.

In the modern, deep-sea environment of ODP Site 959, Ivory Coast-Ghana Marginal Ridge (eastern equatorial Africa) most of the highly reactive, (nano)particulate ferrihydrite input was directly used to form early diagenetic Fe(III)-smectite, glauconite-smectite (Gl-S) and finally evolved glauconite minerals (Baldermann et al., 2013). The latter phases occur together with late diagenetic pyrite overgrowths. We present here new rates of iron sequestration attributed to deep-water glauconitization and pyritization, based on combined electron energy-loss spectroscopy data, high-resolution transmission electron microscopy images and chemical composition data of separated green grain sub-fractions and bulk sediment samples that were taken from the top 25 m of sediments. In the near-surface sediments (≤3 mbsf) iron uptake related to green-clay authigenesis ranged from 23 to 204 µMFe/cm²/ky (76 µMFe/cm²/ky on average), which is 3 to 37 times faster (10 times on average) than that of the pyritization reaction (2 to 29 µMFe/cm²/ky). During advanced stages of early diagenesis (≥5 mbsf) pyritization becomes more important (28 to 131 µMFe/cm²/ky) but iron sequestration by glauconitization remains 1 to 5 times faster (36 to 167 µMFe/cm²/ky with an average rate of 72 µMFe/cm²/ky). Our observations clearly reveal that green-clay authigenesis significantly limits the iron bioavailability in modern, deep-sea sediments and should be considered in future models of the marine iron cycle.

Baldermann, A., Warr. L.N., Grathoff, G.H. and Dietzel, M. (2013) The rate and mechanism of deep-sea glauconite formation at the Ivory Coast - Ghana Marginal Ridge. *Clays and Clay Minerals*, **61**, 258-276.

Controlling factors of alteration rate of basaltic glass and palagonite formation in pillow lavas from Hawaii Scientific Drilling Project

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In submarine flows of the dormant volcano Mauna Kea on Hawaii rapid cooling of magma by seawater resulted in the formation of glassy rims on pillow basalts. In comparison with crystalline basalt, the glassy phase is much more susceptible for chemical weathering due to its isotropic properties. The alteration product of volcanic glass due to interaction with water is palagonite, which is in initial stages of formation amorphous and is getting crystalline with age [1]. Different alteration textures were observed in submarine glasses, some of them interpreted as potentially biogenic [2]. Microorganisms mining glass for nutrient acquisition affect mineral solubility, weathering micromorphology and formation of secondary minerals. Palagonite layers have strong influence on transformation of glasses to crystalline phases and may act as a diffusion barrier slowing down glass alteration. Due to polymerization and precipitation reactions such a barrier may change over time affecting porosity and permeability. Here we determined the relationship between glass alteration and palagonite properties, including petrographical investigations, characterization of pore system, analyzes of glass properties and determination of ionic effects on glass dissolution.

Pore volume of palagonite samples are strongly dependent on the amount of glass preserved, presence of phenocrysts and quench crystals. High shares of pores are between pore radii from 2 to 10 nm due to the presence of smectite. Excellent preserved microbiological morphologies on glass surfaces and in palagonite sheets allowed detailed insights in the nature of microorganisms involved. Open spaces between palagonite sheet and glass indicate a dissolution-reprecipitation-mechanism of glass alteration, supporting a pronounced redistribution of elements during glass dissolution. Microbial alteration seems to be driven by various nutrient and energy sources. The knowledge of these factors is important for understanding, prediction and modeling of microbial activities and their consequences on micromorphology, mineralogy of secondary phases and element turnover in different geologic environments.

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Petrography and crystal-chemistry of authigenic beidellite in the Eocene sandy sediments of the Chu-Saryssu basin (Kazakhstan)

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The chemistry of authigenic smectites is well known to have an impact on diagenetic mineral transformations during the basin evolution (crystal chemistry and crystal structure of mineral phase, rate of mineral reaction). There is a dramatic lack of data concerning the crystal chemistry of dioctahedral smectites, which are precursor materials involved in the illitization process within sandstone reservoirs. Most of the data in the literature concerning smectite crystal-chemistry were recorded on mudstones, shales and bentonites and indicate that illitization proceeds via a montmorillonite-to-illite conversion.

A petrographical and mineralogical investigation is performed to constrain the nature of the authigenic smectite from Eocene sandy sediments of the Chu-Saryssu basin (Kazakhstan). XRD (using the Hofmann-Klemen test), FTIR investigations and chemical microanalysis outline the predominant beidellitic nature of the authigenic smectite. Crystal-chemical investigations indicate a rather homogeneous chemical composition of the smectite at a regional scale leading to the following structural formula:

$(Si_{3.65}Al_{0.35})(Al_{1.65}Fe^{3+}{}_{0.21}Mg_{0.14})O_{10}(OH)_2\,Na_{0.10}Mg_{0.11}\,Ca_{0.04}\,K_{0.07}$.

The fact that beidellite and not montmorillonite is formed primarily in the unconsolidated sandy sediments could have a major impact on the rate of the further illitization in the Chu-Saryssu basin. According to its tetrahedral layer charge, beidellite is a better candidate for a fast conversion into illite. The occurrence of this mineral in early diagenesis of sandy sediments could have a role on the different illitization rates currently observed between sandstones and shale formations in the same basin.

Weathering, sedimentary, and diagenetic controls of mineral and geochemical characteristics of the vertebrate-bearing Silesian Keuper

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Mudstones and claystones from the southern marginal area of the European Upper Triassic mid-continental Keuper basin (Silesia, southern Poland) were investigated using XRD, organic and inorganic chemistry, SEM, K-Ar of illite-smectite, AFT, and stable isotopes of O and C in carbonates.

The K-Ar dates document a post-sedimentary thermal event, 164 Ma or younger. The maximum paleotemperatures are estimated from illite-smectite as ca. 125 °C. Apatite fission track data support this conclusion, indicating an age range of 200-160 Ma at maximum temperatures close to 120 °C, followed by prolonged period of elevated temperatures. Organic maturity indicators suggest maximum paleotemperatures <110 °C.

Palygorskite was identified as authigenic by crystal morphology (TEM), and calcite by its accumulation in soil layers and by its isotopic composition evolving with time, in accordance with the sedimentary and/or climatic changes. Dolomite isotopic composition indicates more saline (concentrated) waters. Palygorskite signals a rapid local change of sedimentary conditions, correlated with algal blooms. This assemblage of syn-sedimentary formed minerals indicates arid climate and the location at the transition from alluvial fan to mud flats.

Fe-rich smectite, kaolinite, and hematite were products of chemical weathering on the surrounding lands. Kaolinite crystal morphology and ordering indicates a short transport distance. Hematite crystallized also in situ, in the soil horizons. A large variation in kaolinite/2:1 minerals ratio reflects hydraulic sorting, except of the Rhaetian, where it signals a climatic change, i.e. a shift in the weathering pattern towards kaolinite, correlated with the disappearance of hematite. The documented hydraulic sorting indicates that in more central parts of the Keuper playa system, where an intense authigenesis of the trioctahedral clays took place, illite and smectite were the dominant detrital clay minerals.

Cr/Nb and Cr/Ti ratios were found as the best chemostratigraphic tools, allowing for the correlation of all investigated profiles. A continuous decrease of these ratios up the investigated sedimentary sequence is interpreted to reflect changes in the provenance pattern from more basic to more acidic rocks.

On the measurement of the Kübler index

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The Kübler index (KI) of “illite crystallinity” has been widely used in diagenesis and very low grade metamorphism researches since 1970s. The procedures of sample treatment for KI measurement was suggested by Kisch and the calibration with standard set had been carried out by Kübler (1990), by Kisch (1991) and by Warr & Rice (1994). It lets all measured “illite crystallinity” data become comparable in a certain level. However, there still remain some aspects causing KI value variations. This study discusses those problems arisen from KI measurement.

Diffractometers/background Chart-record diffractometer records a diffractogram by going paper with ink-pen drawing; its FWHM is counting in mm originally and can be converted into °Δ2θ. Its background is often drawn in a downward curve. This way let the FWHM be measured in a lower level or the KI is relative larger. The digital diffractometer records a diffractogram by two set values; one is the diffraction angle °2θ and the other the intensity. Digital diffractometer deals with background in mathematic ways and produces a straight line or upwards curves for rational calculation reason. It gives a relative narrower FWHM or smaller KI.

Slit settings Different slit settings produce various FWHMs and KI values for the same sample though their deviation is not large. Generally the larger the slit setting is, the larger the irradiation length/area, and the wider the FWHM.

Resolution/defocus Any diffractometer pursues a high resolution for the purpose of finding all reflections, this lets the alignment system be adjusted in a good focus setting. However, once the alignment failed to be the good focus setting, defocus will occur and the resolution will decrease and hence the FWHM will become larger.

Domain size There is a boundary domain size in the Scherrer’s equation beyond which the reflection will begin broadening. This boundary domain size is 1000 Å for Debye-Scherrer optics and 3000 Å for high resolution diffractometer mentioned by Klug & Alexander (1974). In other words, KI is able to monitor those variations in illite’s basal reflections being of a thickness less than 1000 Å for Debye-Scherrer diffractometer and 3000 Å for high resolutional one along direction c* respectively.

Clay minerals in hydro- and geothermal systems

Microwave-assisted hydrothermal synthesis of the lizardite-nepouite series and the kerolite-pimelite series

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Ni-containing silicate clays from the lizardite-nepouite series (1:1) and kerolite-pimelite series (2:1) were successfully synthesized with the microwave-assisted hydrothermal synthesis method. These series were obtained from co-precipitate gels with $Si_2Mg_{3-x}Ni_xO_7.nH_2O$ and $Si_4Mg_{3-x}Ni_xO_{11}.nH_2O$ (x = 0, 0.5, 1, 1.5, 2, 2.5 and 3) compositions. Syntheses were performed at 220 °C during 48 hours under equilibrium water pressure using microwave furnace. X-ray diffraction revealed pure 1:1 and 2:1 silicate clays for the lizardite and the kerolite series, respectively, as it was obtained for conventional hydrothermal synthesis under the same temperature and time conditions. However, the kerolite-pimelite series (2:1) synthesized by microwave exhibited a lower amount of stacked layers than conventional syntheses. The distribution of octahedral cations was controlled by Fourier transform infrared spectroscopy in both near and mid infrared regions. A random distribution of Ni and Mg cations in the octahedral sheet of silicate clays was observed.

These two series of Ni-containing silicate clays are potentially interesting for industrial uses (catalytic processes, nanocomposite applications…).

The Fe-Mg-saponite solid solution series – a hydrothermal synthesis study

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Although the boundary conditions of saponite formation are generally considered to be well known, significant gaps in knowledge still persist how the solution chemistry, temperature and reaction time influence the mineralogy, crystallinity, stability and chemical composition of ferrous saponite.

We synthesized ferrous saponite and Mg-saponite in Teflon-lined, stainless steel autoclaves within two to seven days at temperatures of 60 °C, 120 °C and 180 °C, alkaline pH, reducing conditions and initial solutions with distinct molar Si:Fe:Mg ratios of 4:0:2, 4:1:1, 4:1.5:0.5, 4:1.75:0.25, and 4:1.82:0.18. X-ray diffraction, high-resolution transmission electron microscopy as well as infrared spectroscopic and thermo-analytical analysis of the received precipitates confirmed the nature of the clay minerals to be trioctahedral ferrous saponite, with small admixtures of co-precipitated brucite, opal-CT, 2-line ferrihydrite, and nontronite as the probable alteration product of ferrous saponite. The compositions of the synthetic saponites were highly variable, $(Na_{0.44\text{-}0.59}K_{0.00\text{-}0.05}Ca_{0.00\text{-}0.02})(Fe^{2+}{}_{0.37\text{-}2.41}Mg_{0.24\text{-}2.44}Fe^{3+}{}_{0.00\text{-}0.28})\Sigma_{2.65\text{-}2.85}[(Fe^{3+}{}_{0.00\text{-}0.37}Si_{3.63\text{-}4.00})O_{10}](OH)_2$, but in accordance with naturally occurring trioctahedral Fe and Mg end members, except for the Al content. This suggests the existence of a complete solid solution series of Fe-Mg-saponites (Baldermann et al., in press).

Based on the experimental solution data and solid phase compositions a conceptual reaction sequence for the formation of ferrous saponite was developed. At pH ≥10.4, brucite-type octahedral sheets were formed, which served as a template for subsequent condensation of dissolved Si-O tetrahedrons. Incorporation of Fe(II) in the octahedral template sheets via isomorphic substitution is suggested to stabilize the saponite structure, explaining (i) the abundance of saponite enriched in ^{VI}Fe(II) at elevated Fe supply and (ii) the effect of structural Fe on controlling the net formation rates of ferrous saponite.

Baldermann, A., Dohrmann, R., Kaufhold, S., Nickel, C., Letofsky-Papst, I. and Dietzel, M. (in press) The Fe-Mg-saponite solid solution series - A hydrothermal synthesis study. *Clay Minerals*.

Distribution of clay minerals in technological ores of the Biely vrch Au-porphyry deposit, Slovakia

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The Biely vrch deposit contains a new type of economic gold porphyry mineralization that was recently discovered in the NE part of the Central Slovakia Volcanic Field. The rocks contain here significant amount of hydrothermally originated clay minerals. Advanced (kaolinite) and intermediate (illite and illite-smectite) argillic alteration largely overprinted earlier K-silicate alteration at shallow levels. Intermediate argillic alteration (smectite, I-S, chlorite-smectite, chlorite) overprinted Ca-Na silicate alteration at deeper levels of the porphyry system (Koděra et al., 2010). The exploration company EMED Slovakia allocated four technological ore types. Primary ore is mixture of altered diorite porphyry by K-silicate and argillic alteration in variable ratios. Argillic ore is characterized predominantly by advanced argillic alteration. Oxide ore is situated in near surface zone with variable amounts of Fe oxides and clays. Transitional ore is mixture of previous three types in variable ratios. Primary and transitional ore had significantly lower gold extraction yields of 57-63 wt.% after milling to less than 12.5 mm and cyanide leaching than oxide and argillic ore with yields of over 85 wt.% (AMC, 2010). The primary ore contains no kaolinite, but 10 to 36 wt.% of 2:1 dioctahedral clays. On the other hand, the argillic ore is dominated by kaolinite group minerals (up to 70 wt.%) with minor amounts of 2:1 dioctahedral clays. The transitional and oxide ores have an intermediate position with respect to clay mineral distribution between the above mentioned ore types. Our study shows that the presence of expandable clay minerals decreases gold recovery.

The authors are grateful to the Slovak Research and Development Agency for the
support of the project APVV-0537-10, Operational Programme Research and Development for the support of the project Centre of Excellence for Integrated Research of the Earth‘s Geosphere (ITMS: 26220120064) and EMED Mining, Ltd. for providing of samples and data.

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Characteristics and timing of clay mineralization in the Carboneras and Palomares Fault Zones (SE Spain)

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The Carboneras and Palomares Fault Zones (Trans-Alboran Shear Zone, SE Spain), located in an arid climate and recently exhumed, provide a good opportunity to study clay mineralization and its relation with fault behaviour.

This research is focused on faulted schists and their respective protoliths ascribed to the Alpujárride nappe (Betic Internal Zones), which have been sampled in two major fault zones. In both areas we observed wide zones (≈200 m thick) of fault gouges, and protolith showing a complex arrangement of sheared lenses along fault strand cores.

X-ray diffraction and electron microscopy (SEM/EDX and TEM) show the samples (crystalline protolith and fault gouges) to be dominated by phyllosilicates (chlorite, micas and kaolinite), quartz and Fe and Ti-oxides. Back scattered electron images show irregularly orientated stacks of phyllosilicates with curved shapes in the fault rocks and quartz grains deformed by brittle fracturing. Clay fabrics in the damaged rocks are poorly developed. Lattice images from the protolith sample show defect-free dioctahedral mica (muscovitic and ferrimuscovitic) and Fe-rich chlorite packets, which are generally >1000 Å thick. In addition, chlorite packets include 10 Å layers forming damaged packets less than 150 Å in thickness, probably reflecting the reaction of biotite to chlorite. In the fault-damaged samples phyllosilicates grains are thinner, but their chemistry is similar.

Grains-size fractions from two samples were dated using the illite age dating technique. The age of the authigenic component in both is ≈12 Ma, while the protolith clays are ≈25 Ma. The authigenic ages overlap the ages from Cabo de Gata volcanic series, which formed between 13 and 6 Ma (Rutter et al. 2012). We conclude that the faults were significantly altered by hydrothermal fluids related to volcanic activity, resulting in extensive phyllosilicate enrichment in both fault zones. The mechanical processes related to strike-slip movement along the fault zones, mainly by brittle fracturing, generated the original fault gouges. The existence of unusually thick fault zones here is due mostly to clays generated by igneous fluids, which used the fault zones as conduits that resulted in that were favourable for clay growth.

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Fraipontite in the hydrothermally overprinted oxidation zone of the Preguiça mine, Southern Portugal

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The Preguiça mine is a carbonate-hosted nonsulfide zinc deposit situated in the Magnetitic-Zinciferous Belt of the Ossa-Morena-Zone, Southern Portugal. The metamorphosed primary Zn-Pb sulfide mineralization is hosted by Lower Cambrian dolomite marbles and suffered a supergene oxidation in the upper 90 m during the Tertiary. In the porous, goethite-dominated gossan a variety of secondary minerals including willemite, mimetite, descloizite, cerussite, plattnerite and very rare smithsonite occur. Travertine-like masses of calcite and in part zincian dolomites, as well as massive white clay in the brecciated gossan are conspicuous.

Thirty clay-bearing samples were analyzed using XRD and in part by ATR-FTIR and ESEM with EDX. The rare trioctahedral 1:1 Zn clay mineral fraipontite was identified as the dominant component in all analyzed clay samples with minor amounts of halloysite, quartz, APS-minerals, goethite and hematite. The chemical compositions of the sample material range from 17 - 33 wt.% SiO_2, 44 - 58 wt.% ZnO, 9 - 14 wt.% Al_2O_3 and 1.8 - 8.2 wt.% Fe_2O_3. EDX analyses of fraipontite reveal notably lower alumina contents whereas silica and zinc contents are higher than values reported for fraipontite from other locations. FTIR spectra of fraipontite resemble those from the type locality Moresnet, Belgium. However, splitting of the principal Si-O stretching band (984 cm^{-1} and 935 cm^{-1}) may indicate a low level of tetrahedral Al-for-Si substitution in accordance with the low measured alumina contents. The OH deformation band can be resolved into two overlapping bands at 650 cm^{-1} and 615 cm^{-1} and may indicate partial occupancy of octahedral sites by iron.

Stable oxygen isotope data of secondary carbonates (calcite, zincian dolomite, smithsonite and cerussite) and willemite clearly indicate the involvement of low-temperature hydrothermal fluids at Preguiça. The carbon isotope data of all secondary carbonate minerals are constant and low (-11.0 to -8.3 ‰ V-PDB) indicating the absence of carbon from the marine carbonate wall rocks or the atmosphere. Elevated temperatures and low pH may have promoted the formation of fraipontite and willemite instead of the more common supergene Zn minerals sauconite and hemimorphite.

Genesis of hydrothermal alteration at the Kişladağ porphry gold deposit region, Gedikler, Uşak (Western Anatolia), Turkey

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Hydrothermal alteration is widespread in Pliocene volcanites at the Eşme (Uşak Province). The alteration developed within the Middle-Late Miocene-Pliocene andesitic lava, latite-andesite, tuff, tuffite and agglomerate. Feldspar is argillized and sericitized, biotite and hornblende are opacitized, groundmass is argillized and Fe-oxide/hydroxidized. In Gedikler area, kaolinite±halloysite locally coexist with illite, smectite, gypsum, barite, quartz, calcite, feldspar, hornblende, dolomite, pyrite, alunite and locally jarosite. Gypsum, barite, alunite, locally jarosite and pyrite, native gold, goethite, psilomelane, rutile, sphene, goehite, lepidocrocite associated with argillisation, sericitization, carbonatization, propylitisation, and silicification increase toward the Kışladağ porphry gold deposit. SEM images reveal that rod-like halloysite, platy kaolinite, and flaky smectite edge degraded volcanogenic materials. Depletion of MgO, Na_2O, K_2O and decrease of SiO_2/Al_2O_3 ratios during hydrothermal alteration resulted developement of kaolinite under acidic condition. Enrichment of large-ion lithophile elements and light rare-earth elements, and depleted in high-field-strength elements and heavy rare-earth elements with respect to primitive mantle and chondrite, and are characterized by distinct negative Eu anomalies reflect fractional crystallization of feldspar and amphibole. The H and O isotopic composition and formation temperatures of kaolinite and illite based on meteoric water (-4.5 ‰) yield 33-170 °C and 123-132 °C, respectively revealing development under epithermal alteration processes. The negative $\delta^{34}S$ and possitive $d^{18}O$ values for jarosite and gypsum also suggest steam-heated hydrothermal environment originated from the oxidation of H_2S at or below the water table of the study area or oxidation of pyrite.

This study was supported financially by the Scientific Research Projects Fund of Eskişehir Osmangazi University in the framework of Project 200715009.

3D correlation of chemical elements (K, Ca, Na, Mg, Fe, Al) with recorded mineral composition and alteration zones at Biely vrch porphyry Au deposit, Slovakia - Preliminary results

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The Biely vrch deposit is a new economic Au-porphyry mineralization discovered in Slovakia. The deposit is located in the central zone of the Neogene Javorie stratovolcano, situated in the eastern part of the Central Slovakian Volcanic Field.

Based on the results of preliminary research it is known, that parental intrusion is intensively affected especially by intermediate argillic alteration that replaces K-silicate and in deeper parts Ca-Na alterations. Zones of advanced argillic alteration are the uppermost part of porphyry system and the youngest alteration. They are spread from surface to depth of several hundreds metres in shape of ledges (Koděra et al., 2010). In previous research in this area has been recorded relatively high levels of kaolinite (33 wt.% in average) what represents a possible economic potential of using this clay material as a secondary product of the surface gold mining (Jánošík et al., 2013).

Characterization of the mineral composition of the alteration zones was performed by X-Ray diffraction analysis (oriented clay fraction and randomly oriented bulk fraction) with aim to provide more qualitative and quantitative data to assess the potential of clay exploitation as a secondary product in the exploitation of Au on Biely vrch deposit.

3D correlation of chemical elements (K, Ca, Na, Mg, Fe, Al) with recorded mineral composition and alteration zones showed interesting results. Based on this results we were able to determinate shapes of alteration zones.

The authors are grateful to the Slovak Research and Development Agency for the support of the project APVV-0537-10, *Grant* of the *Comenius University* No. *UK*/300/2013 and EMED Mining, Ltd. for providing of samples and data.

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Glauconitic laminated crusts caused by hydrothermal alteration of lower jurassic pillow-lavas mediated by microbial activity

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Two types of crusts have been described infilling the spaces among pillow-lavas from the Lower Jurassic Median Subbetic (Betic Cordillera, S Spain): a) green laminated crusts and b) black crusts and lentils. A detailed textural and mineral study has made possible to establish the genetic conditions and phases of the infilling, while also interpreting the possible influence of microbial activity in the origin and growth of the laminated crusts. Green crusts show an exceptional laminated morphology and are mostly composed by glauconite ($Si_{3.79}Al^{IV}{}_{0.21}Al^{VI}{}_{0.47}Fe_{0.98}Mg_{0.54}K_{0.65}Ca_{0.11}$) and celadonite ($Si_{3.88}Al^{IV}{}_{0.12}Al^{VI}{}_{0.70}Fe_{0.62}Mg_{0.69}K_{0.87}Ca_{0.04}$), and a minority by smectites. Black crusts and lens-shaped nappes are essentially saponitic ($Si_{3.69}Al^{IV}{}_{0.31}Al^{VI}{}_{0.15}Fe_{0.60}Mg_{2.28}K_{0.01}Ca_{0.10}$). The record of filaments and coccoid-shaped forms from the glauconitic crusts at microscale indicates the potential implication of chemoorganotrophic microbes in the precipitation of the glauconite, and the development of laminated textures under low-temperature hydrothermal conditions. This record is relevant because glauconite is mainly reported as peloidal grains in volcanic-hydrothermal and sedimentary-diagenetic environments but never before has been described forming laminated crusts associated to spaces between pillow-lavas. SEM-BSE images show very small glauconitic lath-like crystals randomly arranged (<1 mm length) making up the inner part of the filaments, and larger celadonitic lath-like crystals oriented perpendicular to the filament (>5 mm length) composing the outer coating.

During an early stage, alteration of pillow-lava edges caused by hydrothermal reducing fluids resulted in black films of saponite and calcite. Later, green laminated crusts composed by glauconite and celadonite grew under oxic conditions due to both circulation and diffusion of oxygenated sea-water along inter-pillow spaces, and the chemoorganotrophic microbial activity under cooler conditions. Finally, and as a consequence of the deposition of marine sediments over the pillow-lavas, a new stage of saponite formation with calcite occurred under higher T and confined/reducing conditions. As the latest products, calcite and quartz are closing the remaining space (or producing geodes) among the pillow-lava bodies.

Clay mineralogy in Bahariya area, Egypt – hydrothermal implications on fault-related iron ore deposits

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The interpretation of the geologic evolution of the northern part of the Bahariya Depression is more or less controversial. The stratigraphic succession of this area comprises Lower Cenomanian siliciclastic rocks with abundant iron horizons (Bahariya Formation) that are overlain unconformably by Middle Eocene carbonates (Naqb Formation). The latter is characterized by localized occurrence of iron ore bodies at El Gedida, Ghorabi and El Harra areas. They show a spatial relation to the main faults of the area. Two sections were studied at Ghorabi and El Harra areas, where the Bahariya Formation is overlain by the ironstone deposits. A third one was studied at Gabal El-Dist where the Bahariya Formation is overlain by Naqb Formation, which is barren of iron in this location. In this paper, insight provided from the study of clays in the Bahariya Formation is used to ascertain the role played by diagenetic and/or hydrothermal processes in the formation of iron ore deposits in the area.

Petrographic studies, scanning electron microscopy, electron microprobe analyses as well as bulk mineralogy (X-ray diffraction) of some selected samples (ironstone crusts) from the Bahariya Formation show that the clay minerals comprise 20 to 30% of the whole rock. XRD study of <2 µm fractions in oriented mounts reveals that the clay mineral phases are mainly smectite (iron-rich, di-octahedral), mixed layered illite/smectite (I/S) and subordinate kaolinite. Some palygorskite and sepiolite were also determined. Smectite is present in all the studied sections. Ordered mixed-layered I/S, locally co-existing with smectite, occur towards the top of the Bahariya succession in the Ghorabi and El Harra areas. In contrast, the formation of illite associated with smectite is not observed at Gabal El-Dist.

From the preliminary studies, the vertical evolution of the clay mineral assemblages is interpreted as a result of increasing temperature affecting the top of the succession where the iron deposits occur. This supports a thermal origin for the overlying iron ore deposits hosted in the Naqb Formation by migration of hydrothermal iron rich fluids through faults in the Ghorabi and El Harra areas but not in Gabal El-Dist where the capping Middle Eocene beds are not replaced by iron and the area is not traversed by major faults.

Mineralogy and geochemistry of mineralizations related to subsequent alterations in the Tekirova Ophiolite nappe, Antalya, Turkey

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The Tekirova Ophiolite Nappe belonging to Antalya Unit in the southwest Anatolia contains continuous ophiolite sequence as tectonic slices in different sizes and pyrometasomatic rocks formed of around igneous rock intrusion, and also alteration products. This study aims to determine the origin and evolution of serpentine and accompanying minerals on the basis of mineralogic-petrographic and geochemical properties of the ophiolitic rocks. Three types of subsequent mineralizations are present in the ophiolitic rocks as pyrometasomatism, serpentinization and listwaenitization during the oceanic crust formation, ocean floor spreading and the syn- and post-emplacement, respectively. The primary ophiolitic rocks represents ultramafic (lherzolite, pyroxenite, clinopyroxenite), mafic (gabbro, diorite, diabase), basalt and radiolarite. Pyrometasomatics have typical metamorphic minerals such as scapolite, diopside, pyrope, pistacite and tremolite. The syn-serpentinization rocks are formed of fully serpentinite and the post-serpentinization rocks are of listwaenites (ophicarbonate, ophisilicate, ophioxide). Rock and mineral samples were investigated by the methods of optical microscopy, scanning electron microscopy, X-ray diffraction and geochemical analysis. The serpentine minerals in the serpentinites can be distinguished from each others by morphologies of ribbon-like of antigorite, platy of lizardite and fibrous of chrysotile. The alteration products are of carbonate (calcite, dolomite, aragonite, magnesite, hydromagnesite, hydrotalcite), oxide (brucite, goethite, hematite), phyllosilicate (smectite, illite, chlorite, talc, CV, C-S, I-S), pyrite, quartz, epidote and analcime minerals. Serpentines are represented by three polytypes (clinocrysotile-2M_1, lizardite-1T, lizardite-2H_1). Trace and REE chondrite-normalized values of Fe-lizardite, Fe-tremolite and Ca-hydromagnesite display that these are derived from rocks with similar origin by a significant differentiation. $\delta^{18}O$ and δD values of serpentines and tremolite indicate hypogene-oceanic and supergene-Alpine type of genesis and environments. ~ 200 °C for oceanic serpentines and ~100 °C for Alpine-type ones were obtained by means of tremolite- and serpentine-water oxygen isotope fractionation data.

Clays and clay-sized minerals in soils and young sediments

Fe(III)-precipitates formed by Fe(II) oxidation in water – structure, reactivity and impact on As

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The oxidation of dissolved Fe(II) in aerated near-neutral natural waters leads to the formation of amorphous to poorly-crystalline Fe(III)-precipitates. Due to their high sorption capacity for major and trace elements and their role as immobilizing sorbents or colloidal carriers, these Fe(III)-precipitates profoundly impact the fate of nutrients and contaminants in natural and technical systems.

The structure and reactivity of Fe(III)-precipitates are affected by major dissolved species that interfere with Fe(III) polymerization and precipitation. To study the effects of phosphate (P), silicate (Si) and Ca on the formation and reactivity of Fe(III)-precipitates and on As co-transformation, we synthesized Fe(III)-precipitates by Fe(II) oxidation in near-neutral aqueous solutions over a wide and relevant range in composition. Macroscopic information on precipitate composition and ion uptake is combined with detailed information on precipitate structure and morphology derived from X-ray absorption spectroscopy and transmission electron microscopy [1-3].

Our results show that amorphous Fe(III)-phosphate forms in the presence of dissolved P. In the absence of P (or after P depletion) the concentration of Si relative to Fe determines the type of precipitate forming, with a shift from poorly-crystalline lepidocrocite in the absence of Si to ferrihydrite-type precipitates at molar Si/Fe ratios above 0.2-0.3. In the presence of Ca and P, mixed Ca-Fe(III)-phosphate with distinct structure and reactivity forms. The variations in the type of Fe(III)-precipitate induced by P, Si and Ca are reflected in drastic changes in the extent of arsenate uptake that could not be rationalized without detailed structural information. The new mechanistic insight gained in this work thus contributes to a better understanding of the impact of Fe(III)-precipitates on nutrient and contaminant dynamics in aquatic and terrestrial systems.

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Clay mineral transformations in mangrove soils – kaolinite to Fe-illite via K-S and I-S mixed-layer

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Soils in mangrove forests have very special physicochemical characteristics. They are rich in fine sediment, accumulate much organic matter and are subjected to water chemistry conditions that change daily with the tide. The fine particle size of the sediment contributes to high mineral reactivity. By the combined effect of burrowing animals, that create innumerable water conduits, and the forcing of water through the sediment by the changing tides, large volumes of water with high solute content circulate through mangrove forest soils. As a result of all the above, these soils have a measurable influence in the organic and inorganic budget of littoral waters.

We are studying the clay mineralogy and water chemistry (fractions 2-0.2 and <0.2 µm) of four Brazilian mangrove forest soils (Bragança, Pará state; Acaraú, Ceará state; Santa Cruz, Espírito Santo state; Cananéia, São Paulo state). They all receive continental sediments dominated by kaolinite and Fe oxides. In the mangrove forest the sediments are enriched in Fe-smectite and Fe-rich illite. XRD reveals kaolinite-smectite (K-S) and illite-smectite (I-S), where mixed-layer phases close to end-members are more abundant (e.g., K-S with 90% K is more abundant than K-S with 50% K, etc.). TEM-EDS shows a transformation by progressive Fe uptake into K-S, smectite, I-S and illite, accompanied by an increasing Fe(II)/Fe(III) ratio (from 0 to ~1.7). Consistent with chemical data, analysis of the XRD 060 clay peaks shows major dioctahedral phases with minor components that can be trioctahedral or Fe(II)-rich dioctahedral phases. We could model the relative proportions of mixed-layer phases by assuming that K-S and I-S with 30-70% smectite react faster (i.e., are consumed faster) than other phases. Kaolinite-illite was observed in one soil, where dissolved Fe is the highest.

We interpret the reactions to be triggered by (1) high dissolved Fe(II) generated by anoxic conditions in the organic-rich, water-logged soils, and (2) high dissolved Na-Mg-Ca-K content from seawater. As Fe is incorporated into the clay, partial Fe reduction takes place in water-logged periods. At the I-S stage, this process is fostered by K uptake and layer collapse, which prevents later Fe re-oxidation. The net result is progressive layer charge increase and K uptake (illitization).

Changes of mineral and chemical composition of soils' clay fraction result from microbial complex activation

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Microorganisms are deemed as an important soil component, but their role in formation and changes of soils' characteristics seems underestimated. It's claimed that cyanobacterum commynity increases the quantity of swelling packets in illites (Alekseeva et al., 2009), destruction of iron smectites can occur during microbial redoxreaction. Microbe-induced calcite precipitation is described and has been already used in geotechics (DeJong et al., 2013). The influence of the whole microbial complex on the characteristics of natural soils is still important.

In this study sand and clay soils of Moscow region (Quaternary aqueglacial and cultural layer soils, as well as Cretaceous sands and Jurassic clays) were investigated. Soils were treated once with glucose solution. Before and after the treatment the clay fraction was sampled and oriented mounts underwent X-ray diffraction tests. Ca^{2+}, HCO_3^- ions content as well as pH of soil-water extract were measured.

X-ray diffraction test showed that one of the main components of all soils was disordered mixed-layer illite-smectite minerals (IS MLM), as well as illite, kaolinite and in several samples - smectite, chlorite. Calcite was also diagnosed in several samples. In all samples the same processes occurred. The main changes were described in IS MLM - the quantities of illite interlayers decreased, structure imperfection increased down to amorphisation of clay minerals' crystal lattice. Microbes can consume and disengage K^+ ions that hold illite layers together and other ions. A decrease of calcite content was also discovered.

During respiration of microorganisms carbon dioxide is released. Maximum of CO_2 emanation is described during the 7-10 days of the experiment. CO_2 presence in pore water increases the solubility of calcite, and during the 10-20 days the content of saluted carbonates in soil-water extract is twice as much as in control samples. pH of the solution increases from 7 till 9. Under this condition the disengaging of Al and Si ions might occur.

Alekseeva T.V. et al. Changes of clay minerals under the influence of alcalophylic cyanobacterium community. Microbiol. 2009; 6(78). P. 816-825

DeJong, J.T. et al. Biogeochemical processes and geotechnical applications: progress, opportunities and challenges. Geotechnique, 2013; 4(63). P. 287-301

The driving influence of clay minerals on establishment and functionality of soil microbial communities

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Since microbial communities in soils are key players of ecosystem services it is of great relevance to understand the influence of soil components on the microbiota. Among the various soil components, a special role might be attributed to surface-active clay minerals. We studied the clay mineral effect on the microbial community establishment by using artificial soils varying only in type of clay minerals (illite, montmorillonite) and presence of metal oxides (ferrihydrite, boehmite) or charcoal. Artificial soils received an identical microbial fraction of a natural soil as inoculant and sterile manure as nutrient source. Artificial soils were incubated under constant environmental conditions over more than two years (842 days) with a second sterile manure input after 1.5 years. Soils sampled after one year were subjected to further 70 days incubation with spiked model pollutant phenanthrene to test the influence of the soil mineral composition and charcoal on the microbial response to the spike. Artificial soils incubated for 842 days were also spiked with phenanthrene and amended with plant litter in order to study the response of microbial communities established over the long term as a function of the soil composition. Soils were sampled over the entire incubation period and microbial communities were analyzed by denaturing gradient gel electrophoresis (DGGE) and Pyrosequencing analysis of 16S rRNA gene fragments amplified from total community DNA. The presence of functional genes involved in phenanthrene degradation was studied by PCR-Southern Blot. Clay minerals affected the initial bacterial community formation as observed by DGGE and Pyrosequencing already after 90 days of incubation. The clay mineral influence persisted over the long term while the effect of other soil components, metal oxides and charcoal, decreased after more than one year of incubation. Pyrosequencing revealed various taxa which established depending on the type of clay mineral. Bacteria in illite and montmorillonite-containing soils differed in their response to phenanthrene and litter on a quantitative and taxonomic level. Our results suggest that clay minerals controlled microbial communities and interface formation resulting in different responses to the spikes.

Clay minerals' transformations in permafrost affected soils of Northern Eurasia

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Whereas physical weathering and disintegration of the hard rocks are widespread in the "cold regions", the observations of active chemical weathering were also reported. Transformations of clay minerals, assigned by acidification and gleyzation leaded to changes of mineralogical composition in the soil profiles, were studied on the example of permafrost affected soils (Cryosols) of Northern Eurasia despite the fact that the profiles are characterized by weakly developed pedogenesis. The <1 μm fractions determined by sedimentation with the pipette method were analyzed based on XRD patterns and FTIR spectra. The key plots were located in the different climate conditions from subarctic of the Polar Urals, cold semi-humid of the highlands of the Altai Mountains, cold continental of Central Siberian Plateau, and ultra-continental one of Central Yakutia plain. Summarizing results, the following processes initiated the clay minerals' distribution in the soil profiles: (i) decrease of portion of the most sensitive to acidification smectitic clays due to decomposing / dissolving; (ii) decrease of portion of biotite and chlorite because of transformation to mixed-layer clays, and / or (iii) appearance of amorphous phase in the upper part of profiles. Most of clay minerals in all studied Cryosols of Northern Eurasia are inherited from loose parent materials and / or occur in soil profiles because of intensive disintegration of skeletic material, if any. Thus, Cryosols in whole spectrum of climatic humidity in cold environment of Northern Eurasia are characterized both by inheritance of clay minerals from loose and hard parent materials and dissolution of phyllosilicates, mainly smectites, in upper horizons as a result of the pedogenesis.

Cambrian paleosol of Baltica

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Cambrian Terreneuvian greenish-grey marine clays (Blue-Clay) of the Lontova Formation were deposited in a large epicontinental sea placed between Sarmatia and Fennoscandia shields. The end of the time is marked by a widespread regression and gap in sedimentation, upper surface of the Lontova clays shows evidence of erosion and subaerial exposure with development of paleosol profiles. In this contribution we report composition and paleogeographical interpretation of Lontova paleosol profiles intersected in three deep drill cores in Estonian and Latvian parts of the Baltic Basin and in Moscow Basin. Thickness of alteration zones reaches 10 m below the paleoweathered surface and is characterized by distinct of pale, brownish-olive yellow to pinkish-red mottled horizonation. The parent sediment is a silty clay with illite(illite-smectite)-chlorite-kaolinite clay mineral assemblage. The alteration sequence is exemplified by progressive destruction of feldspar, chlorite and illite-smectite phases in the uppermost part of the profiles and the neoformation of pedogenic kaolinite. Mineralogical and geochemical and microtextural characteristics suggest varying redox conditions under regular or intermittent tidal influence during pedogenesis. Similar pedotypes with acidic soil formation are found nowadays in subtropical/temperate climate zones at extensive shallow marine flat coastal zone conditions in Southeast Australia and Thailand.

Investigation of hydroxy-interlayered clays in a temperate acidic soil under forest using X-ray diffraction profile modeling – beyond the HIS and HIV description

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The moderate acidic conditions (2.5<pH<5) under temperate forests lead to a drastic decrease of the soil cation exchange capacity due to the polymerization of Al-hydroxyl-sheets in the interlayer spaces of expandable clay layers (smectite or vermiculite). Specific clays with hydroxy-aluminium interlayers (HI) are formed and commonly described in such moderate acidic forest soils, such as hydroxy-aluminium interlayered vermiculite (HIV) or hydroxy-aluminium interlayered smectite (HIS). Nevertheless, owing to the complexity of acidic soil clay mineralogy, the crystal structures of both HIS and HIV are still difficult to determine.

The raw material used in this study is the surface horizon of a forest Alocrisol (Breuil-Chenue, INRA, France). Its bulk <2 µm fraction was separated into four sub-fractions (<0.05 µm, 0.05-0.1 µm, 0.1-0.2 µm, 0.2-2 µm) and experimental X-ray diffraction (XRD) patterns of oriented samples were recorded for Ca-saturated sample in both air dried and ethylene glycol states, and for K-saturated sample heated at 110°C. For each treatment, the experimental XRD patterns of the sub-fractions as well as for the bulk <2 µm fraction were reproduced by using X-ray diffraction profile modeling approach (Hubert et al., 2012).

Results from XRD modeling procedure reveal the complexity of the clay mineralogy as ten clay phases are present in the bulk sample. Four of them are randomly interstratified three component mixed-layer-minerals (MLM) with various contents of illite, smectite and HI layers. Among these MLMs, HIV and HIS structures repeatedly mentioned in literature rather correspond to HI-rich MLM containing contrasted contents in smectite and illite layers. Despite their apparent noticeable contribution to the experimental XRD intensities, HI-rich MLMs only account for 15% of the bulk <2 µm fraction. Further analysis of the structure models derived from the XRD profile modeling approach allows determining the respective distribution of HI-layers in the different clay phases and the different sub-fractions of the bulk sample. Finally, an indicator for characterizing the degree of Al-hydroxyl process is proposed and indicates that about two third of the original expandable layers are transformed into HI layers.

Hubert, F. et al. (2012). *Am. Mineral*. 97, 384-398.

Neoproterozoic Baltic paleosol – clay mineralogy and paleoclimatic interpretation

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Clay mineral composition of soils is largely a function of climate and therefore the clay mineral composition of paleosols can be used for reconstructing past environments. In this contribution we study Baltic paleosol, which is characterized by its tens of meters thick alteration profile and particularly well preserved uppermost strongly kaolinitized lateritic horizon [1]. This Precambrian paleosol is located on East-European platform, Baltic Basin and is developed on the 1.9-1.5 Ga crystalline basement and ca 600 Ma basalt flows in central part of the Baltic Basin. Paleosol is preserved under Ediacaran-Cambrian sandstones-claystones, suggesting minimum age of weathering ca. 555-560 Ma. Although the upper part of paleosol profiles is in places eroded, the Chemical Index of Alteration values reach up to >90(97). Mineralogical composition of the paleosol profiles is characterized by kaolinite, hematite and residual quartz dominated uppermost zone, replaced by assemblage of illite, mixed-layered illite-smectite, chlorite and chlorite-smectitein the lowermost zones. Paleosol profiles show enrichment in Al (up to 30 w%) and a slight increase in K which indicates that paleosol is overprinted by diagenetic illitization. Kaolinite-rich soil profiles with Fe-duricrusts are typically interpreted as intense weathering in warm-humid climates.Downward gradual changes from saprolite to saprock and nearly intact soft-friable structure of the paleosol suggests that weathering occurred just prior to the transgression of the Ediacaran deposits into the area c. 560 Ma. At this time however Baltica paleocontinent was drifting at high-to-intermediate southerly paleolatitudes, seemingly in conflict with its lateritic characteristics.

[1] Liivamägi, S., Somelar, P., Mahaney, W.C., Kirs, J., Vircava, I., Kirsimäe, K. (2014). Late Neoproterozoic Baltic paleosol: Intense weathering at high latitude? Geology, 42, 323 - 326.

Transformation of clay minerals in Albeluvisols from the Carpathian Foothills, Poland

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The main aims of the present study were: 1) to determine mineral composition of clay fraction (<2 μm) in Albeluvisols from the Carpathian Foothills in Poland and 2) to determine transformation of clay minerals in these soils. Four soil profiles were selected to the detailed study showing occurrence of fragipan and clear or weak bleaching of the eluvial horizons due to periodic stagnation of water. Natural clays (i.e. without any chemical pretreatments) and clays separated according to standard procedure (i.e. removal of organic matter using hydrogen peroxide and pedogenic oxides using citrate-bicarbonate-dithionite) were studied using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR and FTIR-ATR), and chemical analysis. The obtained results show that swelling clay minerals (i.e. smectite, mica-smectite, mica-vermiculite, and mica-vermiculite-smectite) are the most common clays in clay fraction of the studied soils. In addition, mica, kaolinite, and chlorite are also present. The studied soils are characterized by higher amount of clay minerals in illuvial horizons (fragipan, argillic) in comparison with upper soil horizons (A, AE, E) what is related to translocation of clay fraction down the soil profile (so-called lessivage). The upper horizons (i.e. A, AE, and E) show occurrence of clay minerals, which do not fully collapse to 10 Å after heating at 330 °C and 550 °C and do not expand after glycerol solvation indicating presence of some material within the interlayers. Comparison of XRD patterns and FTIR spectra of clay fraction before and after removal of organic matter using hydrogen peroxide indicates that mainly organic matter is present within the interlayers of clays from the upper soil horizons. However, after this treatment the full collapse of swelling clay minerals was still not observed what probably is connected with occurrence of organic matter, which is resistant to oxidation by hydrogen peroxide or is related to small amount of metal-hydroxy polymers within the interlayers.

This study was financed by the National Science Centre based on decision number DEC-2012/05/D/ST10/00527.

Influence of cropping practices on clay mineralogy – insights from the Morrow Plots experimental fields

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The Morrow Plots were established at the U. of Illinois in 1876 to answer agricultural questions. They are the oldest agronomic experiment fields in the US with a recorded history of cropping practices. The exceptional series of samples thus represent a unique opportunity to investigate both short- and long-term influence of cropping practices on the status of potassium, an essential plant nutriment. As clay minerals represent, together with K-feldspars and micas, a major K reservoir for plants their mineralogy is likely to be impacted by K uptake during plant growth.

In 2012, top soils were sampled from four plots representing continuous corn crops (CC) and corn-oats-fodder rotations (CR), both with and without fertilization.

Discrete chlorite, kaolinite, and chlorite are present in all samples together with randomly interstratified illite-expandable (ill-exp), kaolinite-expandable (kaol-exp), and chlorite-expandable (chl-exp). The relative content of discrete minerals decreases with decreasing size fraction. In all samples, illite and ill-exp dominate the 2.0-0.2 µm fraction, the global proportion of these two contributions decreasing with decreasing size fraction, whereas the relative proportion of kaol-exp increases.

The behavior of illite and ill-exp contributions is most relevant with respect to the fate of K in these soils. When considered globally these two contributions are similar for each fraction of the different samples. The 2.0-0.2 µm fraction of the CR samples is dominated by illite, however, whereas ill-exp dominates in CC samples. The contrast between CC and CR samples is less pronounced for finer fractions.

Illite thus appears most degraded, and possibly transformed to ill-exp, in CC plots compared to CR ones. This effect is enhanced when size fraction is decreased likely owing to the increased specific surface areas of the finest fraction which promotes K uptake by plants. Formation of kaol-exp appears as a major process in these soils and kaol-exp dominates the finest fractions of all samples.

Surface properties of micron- and submicron-sized mineral particles from modern sediments of the Adriatic Sea

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Surface properties of particulates in modern marine sediments influence surface physico-chemical processes such as adsorption and adhesion of variety dissolved and particulate inorganic and organic species. This study reports on surface properties of micron and submicron-sized mineral phases separated from sediments of different marine environments collected along the eastern Adriatic coast. The surface physico-chemical characteristics, i.e., the specific surface area (SSA), the cation exchange capacity (CEC), and the electrokinetic properties were investigated in relation to the size, structural and morphological characteristics of mineral particles, and the presence of organic matter and Fe oxide/oxyhydroxide coatings at their surfaces. The structural and morphological properties of these particles were examined by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM), and metal analyses were performed by high resolution inductively coupled plasma mass spectrometry (HR ICP-MS). The results obtained show that surface properties of mineral phases were related to their size, mineral composition, and the presence of organic matter and Fe oxide/oxyhydroxide coatings at their surfaces. The concentrations of trace metals in these solids are closely associated to their surface properties.

Environmental changes inferred from karst lake sediment geochemistry and clay minerals during the Holocene (Bokanjacko Blato and Lake Vrana near Biograd)

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The multy-proxy analysis of sediment cores recovered in karstic Lake Vrana (11 m) and polje Bokanjacko blato (7,8 m and 23 m) located in northern Dalmatia, provided continuous sedimentary record extending back to last 10 000 years. The integration of mineralogical and geochemical analysis, together with age model based on AMS radicarbon dates, enabled reconstruction of the main environmental changes in the region. The clay fraction of both cores results from the erosion of the siliciclastic material (soils, terra rossa, marl or loess) in the catchments. Deeper parts of the Bokanjacko blato (12.5-23 m) are composed of red clay deposits overlying limestones. On red clays there are yellow loess-like sediments, covered with grey lake sediments. Dominant clay mineral in red clays is poorly crystalized kaolinite which does not intercalate with DMSO, while in minor amounts there are illite and vermiculite. In loess like deposits there are more illite and well crystalized kaolinite, together with vermiculite and poorly crystalized kaolinite. In lake sediments from 7.8-3.85 cm there are smectite, vermiculite, illite and kaolinite, which suggest origin from loess/marl deposits. In the upper part of the core, there is dominant carbonate sedimentation, with very little clay minerals. InLakeVrana, bottom sediments (8.06-11 m) contain smectite, illite and kaolinite, which arise from the erosion of the marl deposits. Higher erosion rates in that interval are result of the environment in which flood plain predominate, with small area permanently covered with water. After 9 100 cal BP the lake could have been formed, after rising the sea level, evident by pure carbonate sedimentation after that period. In the upper sediments (0-8.06 m), there are hydroxyl interlayered vermiculite, illite and kaolinite, which could be attributed to soils (kalkocambisols) and terra rossa dominated in the area. According to palynological data, human impact (deforestation) probably triggered period of increased soil erosion inLakeVrananear Biograd after 6 100 cal BP.

Natural clay-sized glauconite in Neogene deposits of Belgium

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Natural clay-sized glauconite has the same mineralogical composition as sand-sized glauconite pellets but occurs in clay fractions <2 mm. This particular glauconite habit has already been described in soil environments resulting from pelletal weathering but is hardly ever reported in higher-energy sedimentary environments. In the present study, clay-sized glauconite was identified as a common constituent in transgressive Neogene glauconite pellet-rich deposits of the Southern North Sea in Belgium. X-ray diffraction results revealed that the characteristics of the clay-sized glauconite are very similar to the associated glauconite pellets in sand deposits. Both glauconite types consisted of two glauconite-smectite R1 phases with generally low percentages of expandable layers (<30%) with d060 values ranging between 1.513 Å and 1.519 Å. Clay-sized glauconite was not newly grown but formed by the disintegration of sand-sized glauconite pellets which were abraded or broken up during short-distance transport within the sedimentary basin or over the hinterland. Even in an environment where authigenic glauconite pellets are assumed, slight transport over transgressive surfaces is sufficient to produce clay-sized glauconite. Furthermore, clay-sized glauconite can be eroded from marine deposits and subsequently resedimented in estuarine deposits. Clay-sized glauconite is consequently a proxy for the transport intensity of pelletal glauconite in energetic depositional environments and, moreover, indicates reworking in such deposits which lack pelletal glauconite. The enhanced reactivity of clay-sized glauconite compared to pelletal glauconite probably accounts for Fe-rich groundwaters in the Campine of Belgium and might be important in the formation of iron-sandstones.

Clay minerals in the sediments from the Croatian Adriatic shelf

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Clay minerals are carried into the Adriatic Sea mostly by Italian rivers entering from the west, and less by Albanian rivers coming from the east. Their longitudinal dispersion is governed by general cyclonic circulation. Based on the data obtained on the samples collected primarily on the Italian side of Adriatic main clay minerals are illite and smectite, with minor amounts of chlorite, kaolinite and sometimes serpentine (Tomadin, 2000).

The Croatian Adriatic shelf receives small amounts of terrigenous fine-grained sediments due to the largely carbonatic coast with poorly developed network of mostly karstic rivers. Consequently, this region is covered by mixed carbonate-siliciclastic sediments, mostly sands. In order to supplement the knowledge of sources and clay-mineral composition in sediments of the Adriatic, 33 samples of uncommon muddy surface sediments (containing 8 to 46% of <2 µm fraction and 23 to 90% of carbonates) from the Croatian Adriatic shelf were investigated by XRPD. Semiquantitative mineral analysis, illite and montmorillonite "crystallinity" indices determination were performed in order to obtain data complementary to those of Tomadin (2000) for the western part of the Adriatic.

Observed differences in clay and carbonate mineral content of <2 µm fraction of muddy surface sediments reflect hydro-geographic characteristics of sampling area (i.e. sea currents, bathymetry, closeness of river mouths and Italian volcanoes). Based on observed differences, four areas can be distinguished: Northern Adriatic, Middle-Adriatic Depression, Southern Adriatic and the channel area. Obtained data for the Croatian part of the Adriatic correlate well and complement those obtained by Tomadin (2000) for the western part of the Adriatic.

Tomadin, L., 2000. Sedimentary fluxes and different dispersion mechanisms of the clay sediments in the Adriatic Basin. Rendiconti Lincei Scienze Fisiche e Naturali 9/11, 161-174.

Interaction of clay and iron minerals with bacteria during soil and sediment bioleaching and metals releasing

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Heterotrophic bacteria control many environmentally important processes such as the cycling of metals by consummating of nutrients. Addition of nutrients was studied because it is necessary to support the growth of heterotrophic bacteria in contaminated soil and sediment deficient in organic matter. Their activity was also dependent on the mineral conditions present in the medium. This process was accelerated by chelation accompanied with iron enzymatic reduction. The main mechanism of bacterial activities was production of organic acids with mobilization of iron or metals. Bacteria caused decomposition of metals binding deposition as is adsorption on clay and silt, sorption on solid-surfaces like inorganic precipitates (Fe/Mn oxides) and organic matter, coprecipitation with hydroxides, oxides and carbonates of Fe and Mn in soil and sediments. The purpose of the laboratory work was to evaluate the mobility of different heavy metals, namely Cu, Zn, As, and Fe by soil and sediment bioleaching. Significant bacterial activity was observed with indigenous bacteria in Cu, Zn and As extractions during soil leaching and in Zn and As extraction during sediment leaching. Bacterial activity was also investigated by growth on clay-sized minerals from soil and sediment and also on synthetic ferrihydrite. These activities of heterotrophic indigenous bacteria, naturally found in the iron contaminated environment, were affected by changes in the chemistry of the environmental conditions. The XRD analysis confirmed the presence of goethite in sediment and hematite in soil. The iron and metals concentration was much higher in the clay-size minerals of sediment leachates where indigenous bacteria were isolated from and these were compared to the low Fe dissolution effect and the highest metals release of the mixed soil indigenous bacteria in the clay-size minerals of soil leachates. The fact that the bacteria dissolved iron minerals present mainly in sediment demonstrates the importance of mineral type and environmental conditions that affects the activities of indigenous bacteria. This mobilization process of heavy metals could be used in removal of contamination from soil into groundwater as leachates which could be pumped by drilling systems and treated by precipitation for recycling of water.

This work was supported by the VEGA Agency supporting the project 2/0019/09.

Origin of the neoformation minerals in the Çayırhan (Beypazarı-Ankara) volcano-sedimentary lacustrine basin, central Anatolia, Turkey – preliminary results

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The Cayirhan volcano-sedimentary basin is situated at NW of Ankara city, Central Anatolia. The Pre-Neogene aged units such as metamorphics, ophiolites, granites, limestones form the basement. The Kizilbayir Formation of probably Paleocene age, which rests upon the basement rocks, includes red-brown colored marl, sandstone and conglomerate alternations. The Miocene-Pliocene sedimentary sequence consists of eight formations, which are conformably ovelain by each others. The Miocene sequence starts with the Coraklar Formation, which comprises marl, tuff, tuffite, limestone and a mineable coal seam at the upper level. The Hirka Formation includes platy claystone, limestone, marl and tuff alternations; Karadoruk Formation contains limestone; Akpinar Formation comprises chert, limestone and marl alternations; Bozcayir Formation includes red-green colored marl; Acisu Formation consists of green colored marl and rarely gypsum; Kirmizitepe Formation includes silstone, claystone, marl alternations and limestone at the upper level; Softa Formation consists of gypsum (Siyako,1983; Yagmurlu, et al., 1988; Inci, 1991; Besbelli, 2010).

The mineralogical composition and properties of the samples were determined by X-ray diffraction. Mineralogic composition of the units formed from clay minerals, analcime, clinoptilolite, feldspar, quartz, opal-CT, calcite, dolomite, magnesite, gypsum and mica minerals. Illite, smectite, sepiolite, kaolinite and chlorite are the most abundant clay minerals. According to analysis result, potential source of illite and chlorite were seemed detrital origin while smectite were formed from hydrolysis of volcaniclastic materials. Dolomite, calcite and magnesite precipitated directly from the lake water.

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Yagmurlu,F., Helvaci,C and Inci, U., (1988) Depositional setting and geometric structure of the Beypazarı lignite deposits, Central Anatolia, Turkey. International Journal of Coal Geology, 10, 337-360.

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Clay assemblage of sediments from southerwestern and southern sections of Portugal continental shelf

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The provenance, dispersion and deposition of fine grained sediments from north and central sections of Portugal margin is well documented (Oliveira et al., 2002; Abrantes and Rocha, 2007; and references therein) when compared with the southern sections. Clay composition of sediments from continental shelf can provide relevant information concerning their source area and genesis. The southwestern and southern sections of Portugal shelf are dominate by sediments from medium sand to muds (Martins et al., 2012).The main goal of this study is to assess the provenance of the fine grained sediments and to contribute with knowledge of the clay minerals associations of these sections of the Portuguese shelf. Mineralogy of 19 sediment samples was assessed by XRD on random oriented powders and oriented aggregates. Illite and kaolinite crystallinity indices were determined. The identification and semi-quantification of peak areas revealed a mineralogical composition composed by quartz, calcite, feldspars, dolomite, iron minerals, opal CT and phyllosilicates. Two distinct groups of samples can be established: one with a siliclastic basis and a group with samples composed by carbonates and silicates. Illite, smectite and kaolinite are the most representative clay mineral groups.

This research was supported by an individual post-doctoral grant (BPD/UI88/2911/2013) within the project Sustainable Use of Marine Resources - MARES (CENTRO-07-ST24-FEDER-002033), co-financed by QREN, Mais Centro - Programa Operacional Regional do Centro and European Union FEDER.

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Interactions between microorganisms and ferrihydrite-organic matter associations

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The association of organic matter with minerals strongly affects mineral surface properties such as solubility, charge and hydrophobicity. This will influence their reactivity towards nutrients and pollutants, the adsorption of new organic matter, and their interaction with microorganisms.

We produced ferrihydrite-organic matter associations by adsorption and coprecipitation in laboratory experiments. As a surrogate for dissolved soil organic matter we used the water-extractable fraction of a Podzol forest-floor layer under spruce.

Liquid phase incubation experiments were carried out with an inoculum extracted from the podzol forest-floor under oxic conditions at pH 4.8 to quantify the mineralization of the adsorbed and coprecipitated organic matter. These experiments showed that the association with ferrihydrite stabilized the associated organic matter, but that differences in the degradability of adsorbed and coprecipitated organic matter were small. We therefore conclude that coprecipitation does not lead to a significant formation of microbial inaccessible organic matter domains.

Microbial reduction experiments were performed using *Geobacter bremensis*. We observed that increasing amounts of associated OM led to decreasing initial reaction rates and a decreasing degree of dissolution. Reduction of coprecipitated ferrihydrites was faster than reduction of ferrihydrites with adsorbed OM.

Our data demonstrate that the association with ferrihydrite can effectively stabilize labile polysaccharides against biodegradation. Vice versa, these polysaccharides may protect ferrihydrite from reduction by *geobacter*-like bacteria.

Bacteriological investigation of soils under the anthropogenic influence in Croatia

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Illegal dump sites of solid waste are widespread problem in Croatia. They can be the source of pathogenic and moreover multi-drug resistant bacteria, from which these bacteria can be leached from waste by storm water and thus spread in nature.

In the acid paleosol from Istria predominantly composed of illitic material and illite/smectite mixed-layer minerals we reported an incidental finding of viable clinically related multi-drug resistant strain of *Acinetobacter baumannii* in abundance of 80-120 CFU/g. In the paleosol, *A. baumannii* is immobilized on soil particles. The environmental isolate of *A. baumannii* showed similarity with a clinical isolate originating from hospital in this geographic area and was resistant to gentamicin, trimethoprim/sulfamethoxazole, ciprofloxacin and levofloxacin (Hrenović et al., 2014). In two soil samples from Susak island, intestinal enterococci that are indicators of faecal pollution were found in abundance of 23-82 CFU/g. We also found as much as 3.6-4.7 log CFU/g of carbapenem resistant bacteria in the examined soils. Among the carbapenem resistant bacteria *Cupriavidus gilardii, Cupriavidus respiraculi and Pseudomonas putida were confirmed by* MALDI-TOF MS. The prevalence of carbapenem resistant bacteria among total heterotrophic bacteria was 52-64% log CFU. In the leachate of Zagreb´s official landfill 245 CFU/mL of intestinal enterococci and 2.9 log CFU/mL of carbapenem resistant bacteria were found. The prevalence of carbapenem resistant bacteria among total heterotrophic bacteria was 49% log CFU.

The results of our current investigations suggest that soils under the influence of solid waste contain comparable numbers of pathogenic multi-drug resistant bacteria to the landfill leachate. The soils under anthropogenic influence reveal a potential new and significant source of infection with pathogenic multi-drug resistant bacteria.

Hrenović, J., Durn, G., Goić Barišić, A. & Kovačić, A. (2014): First isolation of environmental Acinetobacter baumannii similar to clinical isolate in paleosol from Croatia.- Appl. Environ. Microbiol., 80, 2860-2866.

Complex studies of clay minerals in the Yenisey river

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There were studied the Quaternary sediments of the region close to Krasnoyarsk, whose age is no more than 10 thousand years. The samples were studied by using the scanning electron microscopy, X-ray, Mössbauer spectroscopy methods.

The morphology, size and chemical composition of the particles is shown in Fig.1 and in the table 1.

The three fractions,-namely strong-magnetic (Fe_3O_4- 87.3%, Fe_2O_3 – 0.7%), soft-magnetic (Fe_2O_3- 21.7%) and non- magnetic (FeO – 53.1%, FeOOH – 46.9%)- were extracted by using the magnetic separation method for determining the minerals - magnetization carriers.The isomer shifts and the quadrupole splitting indicate a different local surrounding emitting and absorbing the nuclei and the different valence of iron ions. In addition, there were detected Albite, Ankerite, Orthoclase in the non-magnetic fraction.

Thus, the Mössbauer spectra can identify the types of magnetic minerals in complex compounds. The identification of the iron-containing natural minerals helps to reveal the stability of the residual magnetization in geological time scales.

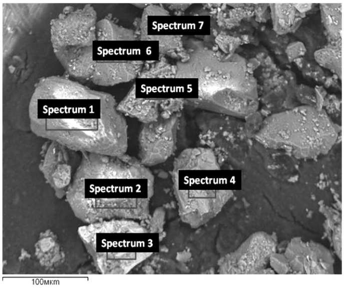
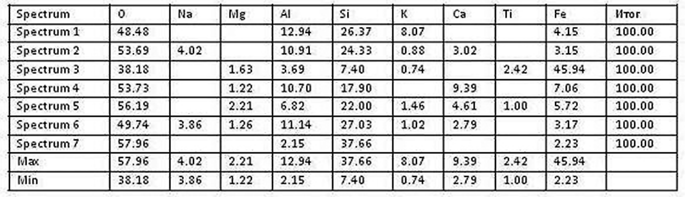


Figure 1. The morphology and size of the particles



Spectrum	O	Na	Mg	Al	Si	K	Ca	Ti	Fe	Итог
Spectrum 1	48.48			12.94	26.37	8.07			4.15	100.00
Spectrum 2	53.69	4.02		10.91	24.33	0.88	3.02		3.15	100.00
Spectrum 3	38.18		1.63	3.69	7.40	0.74		2.42	45.94	100.00
Spectrum 4	53.73		1.22	10.70	17.90		9.39		7.06	100.00
Spectrum 5	56.19		2.21	6.82	22.00	1.46	4.61	1.00	5.72	100.00
Spectrum 6	49.74	3.86	1.26	11.14	27.03	1.02	2.79		3.17	100.00
Spectrum 7	57.96			2.15	37.66				2.23	100.00
Max	57.96	4.02	2.21	12.94	37.66	8.07	9.39	2.42	45.94	
Min	38.18	3.86	1.22	2.15	7.40	0.74	2.79	1.00	2.23	

Figure 2. Elemental composition of particles in weight percent

The role of soil mineral composition in defining Istrian terroir attributes

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A strong debate arises nowadays concerning the concept of terroir, mainly referring to the relationship between soil properties and wine quality. In our ongoing study we investigate soils in three vineyards where Istrian Malvasia, the most widespread cultivar in Istria is grown. Our goal is to compare their mineral composition, physical and chemical properties and to explain how they could indirectly influence wine quality. We present here the first results of our study related to mineral investigation of soils. The studied vineyards are as follows: (1) Monte Coronichi characterised by soil developed on Cretaceous limestone; (2) Sveta Lucija and (3) Grimalda, both characterised by soils developed on Eocene flysch. Terra rossa soil is situated on limestone while two different soils are developed on Eocene flysch, vertic cambisol at Sveta Lucija and eutric brown soil at Grimalda. While terra rossa has the same texture throughout profile (clay), the texture of the other two soils varies from silty clay to loam, creating conditions for better drainage.

The mineral content of these soils differs significantly. Kaolinites, followed by illite, quartz and hematite dominate in terra rossa. Kaolinite which does not form intercalation compounds with dimethylsulfoxide is the dominant mineral in clay fraction which also contains illite, well crystallised kaolinite and mixed-layer clay minerals. The mean value of the Fe_d/ Fe_t ratio in terra rossa, which is taken as an index of weathering is 0.95 and reflects very high degree of weathering of Fe-containing primary silicates. Calcite, followed by quartz, mica and plagioclase dominate in vertic cambisol. Illite is main mineral phase in clay fraction which also contains mixed-layer clay minerals, kaolinites, smectite and vermiculite. The main mineral phases of Grimalda soil are calcite and quartz followed by plagioclase, K-feldspar and mica. Dominant phase in the clay fraction is illite while mixed-layer clay minerals, kaolinites, smectite and vermiculite are sporadically present. Clay mineral content of these soils is in line with cation exchange capacity indicating higher nutrient retention in soils developed on flysch.

Data acquired in this investigation could be used for the appellation, i.e. a legally defined and protected geographical indication, of Istrian Malvasia.

Mineralogical investigation of authigenic aluminum solid phases in acid-stressed forest soils of the Saarland (Germany)

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Soils of temperate- to cool-humid climate zones develop a natural acidity in the course of pedogenesis, which in Central Europe is associated with an additional anthropogenic increase in soil acidity. This results in increasing proteolysis of silicates and in the destruction of clay minerals in strongly acidic surface soils at pH values <5.0. An important feature is the increased mobilization of Al^{3+}-ions, which can precipitate at higher pH values in deeper parts of the soil horizons.

In this study, acid-stressed forest soils of the Saarland (Germany) were analyzed to identify authigenic formed Al phases. For this purpose, mineralogical investigations were carried out on a representative soil profile of the "Schwarzwälder Hochwald" in the area of Weiskirchen in northern Saarland. The analyzed soil samples were taken from a depth of 0 - 90 cm and have pH values between 3.1 (topsoil) and 4.1 (subsoil).

The clay mineralogy of the 0.2 - 2 µm fraction from the different depth levels was investigated using XRD together with additional geochemical analyses from Butz-Braun (2007) and Spooner (2009). Further characterization of individual mineral phases was performed with TEM combined with geochemical (EDX) and crystal structure analysis (SAED).

Based on these investigations chlorite, vermiculite, hydroxy interlayered vermiculite, illite/muscovite and kaolinite, as well as a small proportion of mixed layered minerals were identified. The characteristic occurrence of hydroxy interlayered vermiculites in acidic soil environments were recognized based on their specific $d_{(060)}$-peaks (1.49 - 1.50 Å). The origin of the hydroxyl interlayered vermiculite may be from dioctahedral vermiculite by incorporating of pedogenic formed Al-hydroxy polymers or it can be truely authigenic. Primary chlorites occur, which were altered to vermiculite and kaolinite during soil weathering. The $2M_1$-illite/muscovite present in the entire soil profile is not considered to be authigenic. Further aluminum phases such as gibbsite, imogolite, allophane or jurbanite were not detected in this profile.

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Qualitative and quantitative properties of clay minerals in salt-affected sediments with different organic matter and salt content in the Lake Fehér in Szeged and Kardoskút

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In this paper our research aim was to determine the qualitative and semiquantitative properties of clay minerals from salt-affected young lake sediments with different organic matter (OM) and salt content. For the detailed analysis two alkaline lake system were chosen, (1) Lake Fehér in Szeged and (2) Lake Fehér in Kardoskút, Hungary. 4-meter-depth core samples were taken in three different (spring, summer and autumn) periods always from the same location.

Based on the primary geochemical parameters (alkalinity, salt content, total organic content, grain size distribution and mineralogical composition) six different samples were chosen for the detailed clay mineral investigations. From these samples sub-samples were prepared for the oriented, glycolated and heat treated (350 and 550 ^{0}C) analyses.

The main result of the investigation is that the high salt content (>2 mS) inhibits the presence of expansive clay minerals, whilst in the seams with lower salt content the amount of well-ordered expansive or mixed layer mineral types is definitely higher. A strong relationship is observable between the high alkalinity (pH>10), the rapidly altering water level and the badly ordered clay mineral phases. In every case the smectite group is present in the layers under 1 meter depth, this is the level of the constant ground water table. In the upper 1 meter of the cores smectite group was not detectable.

Based on the results it seems that the salt content and the changes of water levels play the primary role in the formation and transformation of clay minerals, the alkalinity and the organic matter have only a secondary effect. The high salt content, the high alkalinity, the high organic matter content and the repeated wetting and drying processes are mainly responsible for the badly ordered and mixed clay mineral structures.

This research was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP 4.2.4. A/2-11-1-2012-0001 ‘National Excellence Program’ and by the Hungarian Scientific Research Fund (OTKA K-81181).

Clays in geotechnical applications

Development of high density bimodal Bentonite blends for high pressure sealings at the Ibbenbüren coal mine

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In connection with the construction of high pressure water retaining dams at the Ibbenbüren coal mine, a Bentonite-based building material had to be developed. According to the final requirements (see also Wolters et al. in this session) and due to the given circumstances (coal mine - ventilation shaft - wet mine) the development was to fulfill the following standards:
- density of >1.45 t/m³ - preferentially 1.50 t/m³ dry density
- swelling pressure of >0.5 - preferentially 1.0 MPa
- fast emplacement (<10 hours for 150 mt due to water influx)
- self-compacting (no mechanical compacting possible on-site!)

In order to meet these requirements, Bentonite pellets with a grain density of 1.9 t/m³ were filled up with a high flowable sand that had to be able to penetrate the complete package of pellets (figure 1). For delivery, first pellets were loaded and subsequently sand was inserted on top of the pellets directly into the silo truck. The sand completely penetrates the Bentonite filling, leading to a highly homogeneous blend that was blown from silo trucks belowground. The homogeneity of the blend was proved on-site.

Figure 1. Emplacement of the bimodal blend in laboratory

Permeability and swelling pressure of compacted bimodal bentonite blends for underground barriers in Ibbenbüren – Beustfeld

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In the Northern Münsterland, RAG Anthrazit Ibbenbüren GmbH has developed a new exploitation area called Beustfeld in depths of 1200 to 1400 m. The planned exploitation affects two existing high-pressure water-dams. Therefore, two new substituting barriers located at the Bockraden pit in a depth of about 270 m were designed. The substitute for dam 59 is located vertically in the Bockraden shaft directly below the third level. The substitute for dam 71 is located horizontally in the cross-cut of the third level. The load-bearing function is separated from the seal function for the new barriers. The seal function is achieved by a bimodal mixture of bentonite blends (see also Schellhorn et. al. in this session) alternating with sand beds (equipotential material, see also Emmerich et al. in this session).

The sealing was required to exhibit a low permeability of $<10^{-9}$ m/s, homogenous swelling, swelling pressure of 0.5 to 3 MPa at maximum, and the absorption of about 1% volume strain from the exploitation. The permeability of the bimodal bentonite blend mixture was determined to be $4*10^{-12}$ m/s. The equipotential material was designed with a higher permeability to guaranty a homogeneous wetting surface for the bentonite layers (Patentschrift DE 101 49 972 C1).

The swelling pressure of bentonite was determined in laboratory oedometer tests with constant volume regime. The measurements were performed with dry densities from 1.26 to 1.67 g/cm³ and with a water content of about 12-15%. The substituting barriers may undergo a volume strain of about 1%. Hence, the vertical stress was reduced and the remaining swelling capacity was determined for two of the samples. Additionally, the swelling pressure of a bentonite-sand mixture with a ratio of 70:30, according to the used bimodal mixture, was measured.

SANDWICH – multilayer hydraulic sealing system for universal underground application

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The hydraulic sealing element of drift and shaft sealing systems in deep geological disposal systems or underground mining pits is commonly a monolithic construction of compacted bentonite or a compacted bentonite/sand mixture. Inevitable inhomogeneities gained during construction and/or a sudden fluid entry with high hydraulic pressure might cause preferential pathways or even fraction of the hydraulic sealing and enhanced water flow. An innovative multilayer sealing system of bentonite and sandwiched equipotential layers (SANDWICH) supports homogeneous swelling and sealing independent of formation water (Nüesch et al., 2002).

Equipotential layers consist of sandy to silty material characterized by permeability several orders of magnitude higher than the bentonite. Thus, ahead hurrying fluid will be evenly distributed within an equipotential layer and will build up a new homogeneous potential surface for the adjacent bentonite layer.

While functionality was demonstrated with semi-technical scale experiments in vertical and horizontal alignment (HTV-1 to HTV-3) the SANDWICH sealing system is now installed by RAG Anthrazit Ibbenbüren GmbH in the Ibbenbüren coal mine in the vicinity of the Bockraden shaft (see also Wolters et al. and Schellhorn et al. in this session).

In the present contribution we want to illustrate the hydraulic interaction of the bentonite layers with the equipotential layers.

Nüesch, R., Brandelik, A., Hübner, C., & Schuhmann, R. 2002. Verschlussstopfen und Verfahren zum Verschließen von untertägigen Hohlräumen, German patent no. 10149972.

Plasticity and water retention of bentonite-polymer composites

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In recent years, composite materials on the basis of clay-polymer complex formation became of great interest. With its origin in fields of material science focusing, e.g., mechanical improvement of polymeric materials (Fu & Qutubuddin 2001), beneficial composite properties have also been found with respect to geotechnical applications, e.g., bentonite stabilization in landfill lining (Scalia et al. 2014) and reduction of clogging potential during tunneling with earth pressure balance machines (Zumsteg et al. 2013). However, research on composites focusing geotechnical performance exhibit a lack in systematic approaches and thus, general findings on the relationship between composition and macroscopic properties.

This study aims to characterize composite macroscopic behaviour on the basis of its constitutive microscopic characteristics. Since macroscopic clay behaviour is significantly determined by small scale physico-chemical interaction of clay particles including water phase the characterization of hydraulic clay and clay-polymer composite properties is focused.

In this study the influence of polymer addition to Calcigel bentonite on plasticity and water retention was investigated. Therefore, clay-polymer complex formation of Calcigel and cationic, anionic and nonionic polyacrylamide was initiated using solution intercalation method. Each composite was investigated at the maximum adsorption ratio as well as at 10% of maximum adsorption ratio. Water content at liquid, plastic and shrinkage limit as well as composite soil water characteristic curve (SWCC) on the drying path was determined.

Fu, M. & Qutubuddin, S. (2001), ‘Polymer-clay nanocomposites: exfoliation of organophilic montmorillonite nanolayers in polystyrene’, *Polymer* 42, 807-813.

Scalia, J., Benson, C., Bohnhoff, G., Edil, T. & Shackelford, C. (2014), ‘Long-Term Hydraulic Conductivity of a Bentonite-Polymer Composite Permeated with Aggressive Inorganic Solutions’, *Journal of Geotechnical and Geoenvironmental Engineering* 140(3).

Zumsteg, R., Plötze, M. & Puzrin, A. (2013), ‘Reduction of the clogging potential of clays: new chemical applications and novel quantification approaches’, *Géotechnique* 63(4), 276-286.

Limed clay as a replacement for construction sands

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In Belgium, more particularly in Flanders the soil contains of lot of clay, sometimes in combination with loam and/or sand. Due to the limited bearing capacity of clay soils, these soils are not very well suited to be used for foundations of buildings and infrastructure. To improve the properties of clay soils, stabilization with quicklime is often used. This technique was first introduced in the sixties during the construction of highways. The annual use of lime for soil stabilization keeps increasing. In 2012 approximately 1.6 million tons of soil was treated that way. History shows that the lifespan of most buildings and infrastructure is about fifty years. The excavation of clay soils treated with lime will significantly increase in coming years. Flanders is a region with limited availability of natural resources. The Flemish Government stimulates the use of secondary resources to relieve the pressure on natural resources. Excavated clay soil treated with lime can replace natural sand in some applications. This paper presents the results of an investigation on the possibility of replacing sand in construction application by excavated clay soils treated with lime. In the first part properties of normal clay particles are compared with those of limed clay particles. Test results show a significant increase of sand equivalent value and a decrease of methylene blue value. In the second part of the study cement was added to different mixtures as a hydraulic binder. These mixtures were tested on their mechanical properties, such as California Bearing Ratio and compressive strength. The strength development of these mixtures is similar to that of equivalent sand-cement mixtures.

On settlement prediction of reinforced soft clay by a group of stone columns

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The improvement by stone columns increases the bearing capacity of weak soils, decreases their settlement and accelerates their consolidation. Hence, the prediction of stone columns performances should be addressed with respect to all those benefits. This paper studies the behavior of a group of vibro replacement end-bearing stone columns to evaluate the reduction of settlement of reinforced soil. By using a finite difference FLAC3D model, the group of stone columns has been reduced to equivalent co-centric crowns. The obtained numerical results are compared to existing analytical and numerical methods for the prediction of reinforced soil settlement. It was found that the prediction of settlement by the 3D numerical model of equivalent co-centric crowns is less than that obtained by the actual group of stone columns model. This results needs to be validated through comparison between numerical, analytical and in situ measurements of settlement.

On the influence of initial permeability and stiffness on the the cyclic consolidation behavior of soft clays

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Cyclic consolidation processes in soft clays play an important role for a multitude of geotechnical applications, as e.g. considering the consolidation of soft soils under foundations for offshore windcraft plants caused by cyclic wind and wave loading. The objective of the present study is to analyze the time-dependent dissipation behavior of excess pore water pressures during these cyclic consolidation processes in soft soils. The study is carried out on the basis of cyclic oedometer tests on materials with different initial permeability and stiffness under partially drained conditions. It reveals that a time shift between applied vertical load and measured excess pore water pressure arises, which is dependent on the permeability and stiffness of the material. The correlation between the evolution of this time shift and the evolution of stiffness and permeability of the material is evaluated and compared to the results of a numerical analysis of the problem.

Leaching of soil conditioning chemicals from excavated tunnel muck

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The Earth Pressure Balance method (EPBM) became more and more the chosen excavation method for mechanized tunneling in soft soils with a TBM. The support of the tunnel face directly via the excavated material brings various benefits. Along with low settlements at the surface no time and space consuming separation (as for slurry shields) is necessary. Excavation is possible with high advancement rates. One key parameter for the success of the EPBM is the proper handling of the excavated material, namely, environmentally safe transportation and deposition of the excavated tunnel muck.

Often, and especially in clayey soils, the in situ soil conditions require the addition of soil conditioning chemicals (foams and polymers) during the excavation process to guarantee the desired consistency of the soil being able to support the tunnel face in the chamber of the TBM. The necessary conditioning creates a chemically contaminated soft material, whose deposition has to fulfill the environmental regulations. Especially the contamination of the groundwater has to be prohibited.

Evaluation of the concentration of the chemicals arriving in the groundwater is a complex task and the processes are depending on many parameters. The leaching tendency of the chemicals from the treated soil is of major importance. Also the possible dilution and the biological degradation have to be taken into account. These leaching and degradation properties depend mainly on the interaction between the clay minerals and the used soil conditioners, requiring deeper knowledge of the leaching properties of polymer and foam conditioned soils.

To gain more information and to simulate the consolidation and leaching processes of different conditioned clay-sand mixtures in a realistic setup, a series of tests in an oedometer cell were carried out in the laboratory. Percolation of the sample after consolidation allowed collection of the eluate, which was analyzed with respect to the total organic carbon (TOC) as an indicator of the chemical concentration in the leachate. The results show that the amount of leached chemical is dependent both on the predominant clay mineral and on the soil conditioner used. Additionally the permeability of the conditioned samples is considerably changed if compared to the non-conditioned clay-sand samples.

Chemically enhanced drainage as a stabilisation technique for landslides

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Stability of landslides can be increased by providing additional retaining forces and reducing the driving forces. Chemically enhanced drainage is proposed as soil improvement technique for mitigation of unstable slopes. It is based on construction of drainage conduits, which are permeable zones created in-situ by chemically modifying the clay phase of fine grained soils. The underlying mechanism is a cation exchange reaction leading to interlayer fixation and aggregation of clay minerals to silt-sized particles.

The resulting changes in soil fabric and structure were characterized based on observations on the pore and particle scale using mercury intrusion porosimetry and particle size measurements. Additionally the macroscopic effects on mechanical and hydraulic properties were assessed in laboratory experiments. These experiments were used to validate the numerical modelling of the highly coupled phenomenon, where both the advective transport of the chemical and the mechanical behaviour are affected by chemical modification of the hydraulic conductivity. A finite element analysis - which accounted for the different physical processes and their couplings - was carried out with a commercial FE-Code (Comsol Multiphysics).

In a first step, the growth of the modified zone around an injection conduit was examined. By means of a radially symmetrical simulation the transport of the reactive chemical in a temporally and spatially variable flow field could be reproduced. Thereby the characteristics of the chemically enhanced drains were quantified. These findings were then extrapolated in a second step to geotechnical applications of chemical drains. In such large scale boundary value problems the alteration of the groundwater table predominantly defined the mechanical response of the soil. With an effective stress analysis, which accounted for the hydro-mechanical coupling between pore water pressures and shear resistance, the stabilising effect of chemical enhanced drainage on a labile slope could be demonstrated.

The role of meta-clay surface area for binder materials

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All cementation processes are significantly influenced by the binder to grain ratio, however the importance of the specific surface area (SSA), as measured by BET, is often not considered. In this study, we investigated the role of SSA in meta-clay produced from I/S-rich Friedland clay from N Germany, which is currently being investigated for usage as geopolymer cement. Geopolymers are inorganic binders made of alkali activated aluminosilicate materials such as furnace slag or dehydroxylated clays ("meta-clays"). The alkaline treatment leads to dissolution of Al and Si which condenses and polymerises while hardening even under wet conditions, to form a polymer network. Dehydroxylated kaolin (meta-kaolin) is the most commonly used precursor material for geopolymers, but 2:1 sheet silicates such as smectite, mica or mixed layered I/S can also be used. The common assumption made is that the reactivity of the meta-clay is dependent largely on the amount of 5-fold coordinated aluminium and the Al:Si ratio of the reacted material. However, our results show neither the concentration of the 5-fold coordination of Al nor the Al:Si ratio explain the improved hardening properties of the meta-clay powder observed with an increase in the sintering temperature. Instead a clear relationship is revealed between geopolymer cement hardening and a reduction of the SSA. We postulate that enhanced thermal treatment leads to a lower SSA and therefore less cement phase is needed to connect residual grains. The challenge is to find the optimum ratio between SSA and the amount of cement phase produced for different geopolymer precursor materials. This reaction model could explain why some kaolin clays are less suitable for geopolymer cements than others, which show varying particle size distributions and degrees of disordering that result in varying SSA to grain size ratios.

Swelling pressure measurements in black shales with the MENARD pressuremeter

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Many cases of damage are known of constructions founded on the swellable Black Shales (Toarcian), outcropping in the south of Luxembourg and the Belgian and French border regions. Data form 50 years of practice on MENARD pressuremeter testing in Luxembourg in those pyritic shales have allowed to establish a statistical correlation between laboratory and pressuremeter results, identifying hard pyritic shales characterised by a limit pressure p_l >1,2 MPa, as soils with a high risk of swelling. The gathered data enable us to point out the difference between pyritic swell and the heave caused by decreasing stress. Consequently we can say that the pressuremeter is a useful tool for the investigation of pyritic black shales able to induce swell. Furthermore it could be applied to investigate similar black shale facies which can be found all over the world since Paleozoic.

Swelling inhibitors for conservation of Swiss molasse

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Sandstones that contain swelling clay minerals are often found in buildings and monuments of historic and cultural importance. When these sandstones are subjected to cycles of wetting and drying, they can degrade due to strain gradients that develop during these cycles, as these strain gradients lead to stresses on the order of magnitude of the strength of the stone[1,2]. Additionally, commonly used ethylsilicate consolidation treatments are rendered ineffective within just a few wetting and drying cycles, making this conservation treatment not an option for conservators who must deal with these stones[3]. Swelling can be significantly reduced, however, by the use of an alkyldiamine treatment, where the amines substitute into the clay mineral interlayer and reduce the expansion upon subsequent rehydration[1,4].

The molasse sandstones of Swiss plateau are found in numerous historic buildings throughout the country, such as the cathedrals of Lausanne and Fribourg, and as sandstones with a significant amount of swelling clay minerals they exhibit the problems described above. In this work, new polyamine swelling inhibitors are tested on a few Swiss molasse sandstones and demonstrate similar performance to the alkyldiamine treatments. Their mechanism of action is probed via experimental techniques such as X-ray diffraction.

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2. Ruedrich, J., Bartelsen, T., Dohrmann, R. & Siegesmund, S. Moisture expansion as a deterioration factor for sandstone used in buildings. *Environ. Earth Sci.* 63, 1545-1564 (2011).
3. Félix, C. Déformation des grès consecutive à leur consolidation avec un silicate d'ethyle. In Proc. 7th Int. IAEG Congress, Lisboa, September 5-9, R. Oliveira, L.F. Rodrigues, A.G Coelho & A.P Cunha Editors, A.A. Balkema, 5:3543-3550 (1994).
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Amount of water in saturated compacted bentonite samples at various temperatures

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The aim of this work is to experimentally check amount of water in fully saturated bentonite under various temperature (25 °C, 95 °C a110 °C) and dry densities (1.35 - 1.75 Mg/m^3). The degree of saturation was chosen for evaluation as first and then apparent density of pore water was used.

Two Czech materials were chosen for testing: magnesium-calcium bentonite from Rokle deposit and Na-activated bentonite from the same area. The results are expressed as dependencies of degree of saturation/ apparent density of pore water on both dry density and temperature.

The results on both materials showed that the degree of saturation (evaluated according to standard method for soils) at full saturation state increases with dry density and cross the theoretical maximum - value of one. The reason of this behaviour is that some of the pore water in bentonite is strongly bound and its density is higher than for free water. These results are in line with some observation in literature and previous own experiments.

Also dependence of degree of saturation on temperature was observed for both materials. Degree of saturation/ apparent density of pore water increases with temperature for Rokle bentonite but decreases for Na-activated bentonite.

Adobe material of the Sun Temple, Pachacamac, Peru – Engineering, geological classification as a challenge

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A standard engineering-geological classification of fine-grained soils consists of the determination of the grain-size distribution and Atterberg consistency limits - liquid limit w_L (%) and plastic limit w_P (%), with the calculation of the plasticity index $I_P=w_L-w_P$ (STN 73 1001: 2010). In Slovakia, sieving combined with the sedimentation using a Casagrande aerometer is a standard procedure for obtaining the grain-size distribution, requiring at least 80 to 100 g of a clayey or silty sand sample. Another 200 to 300 g are needed for the standard cone test of w_L (BS 1377: 1990). The minimum for an engineering-geological classification would be 300 g of the sample. However, less than 100 g were available from the adobe material of the Sun Temple located in the archeological complex of Pachacamac near Lima, Peru. The 2000 years old site is on the Tentative World Heritage List of UNESCO since 1996 (http://whc.unesco.org, 2014-04-30). For such a small sample, non-standard methods had to be searched for. The grain-size distribution was done by sieving combined with Sedigraph. The water adsorption by Enslin-Neff was used for the calculation of w_L and I_P according to Petkovsek, Macek & Majes (2009). This allowed the sample to be classified as silty sand with 19.5% of fine fraction (silt + clay) of low plasticity, class symbol SM. The result was confirmed by the X-ray diffraction analysis that showed kaolinite as the main clay mineral, no traces of smectite were found. Cosidering the geotechnical impact of the findings, the absence of expandable smectite is very important for the volume stability of the adobe, because the Sun Temple ruins were uncovered and left without any protection against rainfalls. On the other hand, the amount of the cohesive fraction is low, whereby the cohesion of kaolinite is lower than that of smectite, which indicates a low strength of the adobe material.

BS 1377: 1990 British Standard Methods of test for Soils for civil engineering purposes. Part 2. Classification tests.

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The possibility of using non-qualified clay-rich sand by overview the standard (methylene blue test), mineralogy of aggregates, and engineering behavior

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The natural aggregates from quarry are getting exhausted due to the demanding from bloomed construction. Purchasing aggregates or crushing rocks are the short term solutions with high costs by transporting, washing crushed fines, and abandoning non-qualified part. However, we are able to save the natural resource if we do count the accuracy of standard and the performance of engineering behavior. Then, the non-qualified aggregates, which are clay-rich sands, will be used without being wasted. The study aims to overview the limitation and uncertain parameters of European standard for qualifying fine in aggregates (methylene blue test, EN 933-9) with the contribution of kaolinite, illite and bentonite, which are the common minerals in the natural with different properties. The engineering behaviors from these clay in asphalt concrete (AC) are also inspected. Therefore, we are able to modify the requirement of fine aggregates base on its mineralogical contribution, its properties, and its engineering behavior. The result shows the parameters of aggregates for MB test have to be modified for higher accuracy and the high possibility to apply non-qualified aggregates in AC pavement by its engineering behavior.

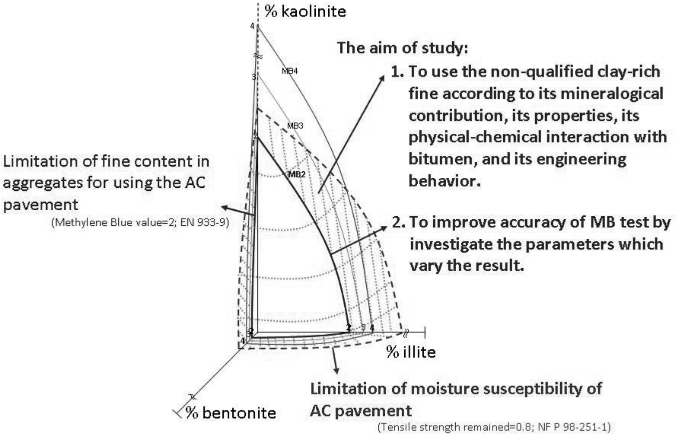

Figure 1. The schematic diagram of the possibility to use non-qualified clay-rich sand by overview the standard (methylene blue test), mineralogy of aggregates, and engineering behavior

Stabilization-potential of bentonite-polymer-mixtures and its use for landfill technology

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Bentonites are often used as barrier materials in landfill technology to prevent infiltration of leachates to the natural environment. Since decades, geoenvironmental engineering aims at improving the hydro-mechanical performance of landfill liners. Various studies on the permeability performance of geosynthetic clay liners (GCLs) show effects of non-standard liquids on behaviour of Na^+-bentonite regarding its sealing capacity. With increasing concentration of chemical aggressive solutions the sealing capacity decreases (Shackelford et al. 2000). An opportunity to improve the hydraulic permeability of the bentonites is the addition of polymers. The changes in hydraulic permeability performance of polymer treated and untreated bentonites while adding chemical aggressive solutions were studied by several authors. Results obtained by Scalia et al. (2014) illustrate that an increase in permeability can be prevented by adding polymer to Na^+-bentonite. On the other hand, Ashmawy et al. (2002) presented results on the incapability of several commercial bentonite-polymer-products.

The objective of this study is to characterize the influence of polymer addition on hydraulic performance of Na^+-bentonite systematically.

The influence of 1% polymer addition of non-ionic, cationic and anionic polyacrylamide on the swelling pressure and hydraulic permeability of MX 80 bentonite was investigated. Preparation of bentonite-polymer-mixtures was conducted (1) in dry conditions and (2) using solution-intercalation method. Experiments on hydraulic permeability were carried out using distilled water as well as CaCl2-solution.

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Clays, reservoir rocks and energy issues

Clay minerals in poresystems of reservoir sandstones

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The presence of clay minerals within the pores of clastic sediments can have both enhancing and deteriorating effects on their reservoir quality, negative effects generally getting dominant and worse during continued burial. Positive effects of authigenic clay include the inhibition of pore cementation due to grain -rimming chlorite, or retardation of cementation (e.g. quartz) due to the cover of grain surfaces by tangential clay coats. Negative effects on reservoir quality, particularly on permeability, are assigned to clay minerals, that are not fixed to pore surfaces and can migrate during induced pore water flow, and block pore throats like minerals of the kaolinite group. Growth of authigenic illite or illite -smectite mixed -layer crystals is expected to be the most frequent and have most deteriorating effect on reservoir flow properties. Not the volumetric amount of particular clay mineral types but their habit, size and textural position are essential for their quality reducing effects. In contrast, intergranular blocky cements like quartz, carbonates, sulfates or zeolites are effective by volume.

There is no general agreement on the mechanisms and controlling factors of sandstone pore illitization. The most common process of illite precipitation in sandstone pores appears to be the consumption of kaolinite in the presence of K -feldspar. There is evidence for Illite growth as a continuous process, as well as episodic in limited time intervals. Uncertainty exists in context to the relevance and geological significance of illite K/Ar - and Ar-Ar-ages, although there exists ample evidence for links between timing of early hydrocarbon migration and periods of enhanced clay growth (indicated by narrow isotopic age spectra) in many basins. Additional aspects in debate are the role of temperature and organics in the neoformation of clays, fluid/rock ratios, open vs. closed systems, and reasons for morphological -textural diversity of authigenic clays. Despite these assumed controversies, there has been considerable progress during the last decades, particularly regarding the importance of clay coats, early diagenetic controls on mesodiagenetic clay formation, and understanding of (alternative) mechanisms of clay growth.

Predrill Reservoir-quality predictive models have relied on empirical correlations or on first -principle geochemical simulations that incorporate laboratory-derived input parameters. Today results of high -quality petrographic analyses are linked in modeling to thermal and effective-stress histories, including the evolution of reactive pore surface areas.

Porosity preservation in deeply buried (8552 m) mudstones of the Vienna Basin (Austria)

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The Vienna Basin is a Neogene pull-apart basin which is situated between the Eastern Alps to the West, the Carpathians to the North-East and the Pannonian Basin to the East. Its principal source rock for oil and gas are Malmian mudstones of the Mikulov Formation. We examined core samples provided by OMV from this unit that were recovered from depths of 8160 m to 8552 m, and studied their microfabrics in argon ion milled samples with a FEI Quanta 400 FEG scanning electron microscope, and quantified their mineralogy with X-ray diffraction (XRD).

XRD analysis shows that the main components of bulk samples are quartz, calcite and clay, and also reveals minor amounts of ankerite, plagioclase and pyrite. The clay mineralogy of these deep samples was quantified with X-ray diffraction through application of the mineral intensity factor (MIF)-method of Moore and Reynolds (1997). The clay fraction of the deep mudstones contains 17-28% illite/smectite (I/S) mixed-layer mineral, 63-70% illiteand 9-13% chlorite. R3 ordering with 90% illite in I/S prevails at these great depths.

Whereas we did not expect to find preserved porosity in samples from such depths, we nonetheless found significant porosity and a variety of pore types of nanometer to micrometer size range. Although the fabric appears tightly cemented and packed at low magnification, phyllosilicate framework pores up to 2 µm are common in interstitial areas between harder grains, and are in places held open because of “clamping” of phyllosilicate platelets by diagenetic cements. Carbonate framework pores of similar size occur in early diagenetically cemented areas. In addition, the margins of calcite grains have in places undergone partial dissolution (probably due to organic acid production during late diagenesis), leading to pores in the 100 nm to 1 µm size range. Organic matter occurs as two broad categories, amorphous and structured. The latter lacks pore development, whereas the former occurs interstitially between other minerals and shows well developed OM-pores (10-500 nm).

Overall, these observations suggest that there is a potential to produce gas from very deeply buried mudstones.

Comprehensive study of clay minerals in section E of Qom formation and Sarajeh gas storage field

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Sarajeh gas storage field is an anticline located in carbonate sedimentary rocks belongs to section E of Qom formation (upper Oligocene and lower Miocene). Main objective of this research is to identify clay minerals on the mentioned area. Representative samples were collected from wells No. 8 and No. 12. In addition to preliminary microscopic studies, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and energy dispersive X-Ray (EDX) were applied for determination of main minerals and detecting clay types. With respect to these studies, major minerals were calcite (over than 50% of total sample volume) feldspar and quartz. With respect to SEM images as quartz and calcite show sharp edges, it was concluded that the minerals were not so far from their depositional environment. Almost all clay minerals were placed as filling between quartz and calcite crystals. Volume of feldspar and quartz were two times more than the total amount of clay minerals. Illite and chlorite were the main clay minerals while minor swelling mixed-layer clays were also present.

Subsequently, open-hole logging data was used for clay mineral determination. These petrophysical analyses confirmed that illite and chlorite were the main clay minerals while minor swelling mixed-layer clays and kaolinite were also present. Using previous proposed kinetics equations and reservoir in-situ data showed the gradual conversion of montmorillonite to illite during diagenesis process. In conclusion, this anticline can be used as a good nominee of gas storage reservoir because of appropriate porosity and permeability in reservoir area.

Mineralogy, chemistry and surface properties of Alberta oil sands

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Mined Alberta oil sands consist of four petrologically different types of ores (marine clays, marine sands, estuarine clay and estuarine sands). The combination of the different types of ores affects the properties of the oil sands and thus bitumen extraction and oil sands processability. It has been shown that clays cause problems in bitumen extraction and effect processability of oil sands. It is thus of great importance to understand the mineralogy, chemistry and surface properties of clays to improve both bitumen extraction and oil sands processability. Four petrologically different types of Alberta oil sands were examined in this study by Dean-Stark analysis, XRD, quantitative XRD, infrared spectroscopy, ICP-MS and C, H, N, S content analysis, SEM-EDX, cation exchange capacity (CEC), layer charge density (LCD) and surface area (SA) measurements. The results showed that the four types of Alberta oil sands consist of quartz, kaolinite, illite, illite-smectite (%S_{XRD} 10±2), chlorite, K-feldspar, carbonates (calcite, dolomite and siderite), TiO_2 minerals (anatase and rutile) and pyrite (Osacky et al., 2013). The quantitative mineralogical analysis correlated well with chemical composition of the oil sands. Bitumen removal was the most effective in the coarse quartz-rich samples. The toluene insoluble organic carbon was associated mainly with the clay minerals. The surface properties were primarilly controlled by the mineralogy of the studied oil sands, mainly by the type and quantity of clay minerals (Osacky et al., 2014). CEC, SA and LCD increased as the amount of 2:1 clays (illite and illite-smectite) increased. The results indicated that illite-smectite may be largely responsible for high CEC, SA and LCD in the fine fractions of Alberta oil sands.

The authors are grateful to the Slovak Research and Development Agency (project: APVV-0339-12) and VEGA 1/0301/14 for funding this research.

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The swelling of smectites by high-pressure CO_2 and the possible impact on the containment of CO_2 below the caprock

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A model has been developed for single phase fluid transport of dissolved CO_2 in brine through a shaly caprock above a CO_2 storage reservoir. The model couples two species convective-diffusive flow with poro-elastic effects. The model includes the adsorption of CO_2 in smectite-rich shale and the associated swelling of this material and their effect on caprock porosity, permeability and stress in the caprock for curl free deformation. The input parameters for the model have been derived from experimental data. In particular, expressions for chemical potentials and partial molar volumes of water and CO_2 in the interlayer space of clay have been constructed from heat of immersion experiments, adsorption isotherms, X-ray and neutron diffraction studies and clay swelling strain and stress measurements.

The model predicts that at typical conditions for an off-shore CCS project, the stresses following from CO_2 adsorption in a smectite containing caprock are substantial. When the rock is under an unfavourable stress condition, local shear failure in caprock exposed to CO_2 may occur in a period of 100 - 10000 years despite that the permeability of the rock may reduce under the increasing compressive stress. Considering the present uncertainties in the experimental data, the present results should be considered as indicative. Anisotropy and the possibilities that the permeability may increase when the stress in the rock is close to shear failure and that non-elastic effects may relax the swelling stress (over long periods of CO_2 storage) have not been included in this work.

Water distribution in montmorillonite as a function of temperature and pressure

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Water confined in narrow pores has significantly different properties than bulk water. Montmorillonite accommodates such water in its interlayer space, up to 100% at low hydration. At higher hydration it coexists with a second water population in the interparticle pores, which has bulk like properties. Understanding e.g. the water diffusion in montmorillonite on the macroscopic scale requires the determination of the ratio of this two water populations.

To this end high resolution neutron spectroscopy (NS) as a novel technique has been applied. The basic idea is the same as in every cryoporometry experiment: water in small pores can be supercooled. Uniqueness and limitations of this method will be presented.

NS results for homoionic Na- and Cs-samples at various water contents have been compared with the amount of interlayer water estimated from the measured interlayer thickness and surface area. At higher hydration large differences between the two methods have been found for both cations. For Na montmorillonite this can be explained by water redistribution during freezing (the interlayer thickness is decreasing to a value corresponding to 2 water layers slightly below 0 degree) [1], and therefore the NS results characterize the samples only at low temperature. Interestingly, in case of Cs montmorillonite NS results indicate about 50% increase of the amount of interlayer water. Counter-intuitive water uptake has also been observed in similar systems upon pressure application [2].

In the case of clay swelling, most hydration studies concern only the relative humidity as a control parameter. In a currently running project the swelling of Na- and Cs- montmorillonite as a function of temperature, pressure and water content is studied experimentally and by computer simulation. First results will be shown.

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Swelling stress development in smectites upon exposure to CO_2 under in-situ p-T conditions

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Regarding CO_2 geological sequestration, when CO_2 diffuses into laterally confined smectite-bearing caprocks, swelling response of smectites due to CO_2 uptake is expected to generate a swelling stress under in-situ conditions. To explore the effect of this self-stressing mechanism on sealing integrity of caprocks, we measured the axial swelling stress developed in smectite aggregates exposed to supercritical CO_2 in a 1-D compaction vessel (oedometer). The experiments were conducted on smectite samples subjected to various initial vertical effective stresses under in-situ p-T conditions corresponding to burial depths of 0.5 to 2.5 km, hence initial vertical effective stresses of 10~30 MPa, and temperatures of 44~80 °C. Samples used were circular discs (diameter=12 mm, thickness=0.6~0.7 mm), derived by pre-compacting of 0.15 g powder of Na-rich Wyoming montmorillonite (SWy-1) at vertical stress of 60 MPa for 4 hours, with the sample being pre-equilibrated with lab air (RH=45~55%), with liquid water at 1 bar, or under vacuum at target experimental temperature. CO_2 introduced to the sample was 10 MPa. Besides experiments conducted with CO_2, a few control tests were performed using Ar instead of CO_2.

The swelling stresses measured in our experiments fall in the range of 5 to 11 MPa, decrease with increasing effective (overburden) stresses, and decrease with temperature. Besides that, wet samples generally develop higher swelling stress than dry ones. For control tests performed by Ar, only 1 to 2 MPa swelling stress develops in air-dry and vacuum-dry samples while the water-saturated samples give rise to significant swelling stress.

The results imply that CO_2 penetration into smectite-bearing caprocks and faults in geological storage systems will in general produce swelling stresses of the order of 5-11 MPa. Increases in normal stress of this magnitude will mainly tend to close fractures and joints in the rock mass affected, thus reducing bulk permeability and increasing seal integrity. However, whether local swelling can generate sufficient shear stress to activate shear fractures, thus reducing sealing integrity, calls for further exploration.

Microfabric of tectonically faulted Opalinus Clay – What can it tell us about deformation mechanisms and fault properties?

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Deformation mechanisms of shear zones in clay often remain speculative, as investigating the internal structure of this thin zones is complicated and as the microstructure can be rather similar for a wide range of deformation mechanisms. We use ion beam electron microscopy and ultra thin section analysis to identify and describe tectonic shear zones in overconsolidated Opalinus Clay (OPA) from the Mont Terri Underground Research Laboratory (CH), a site to evaluate the long-term safty of radioactive waste disposal. We report five structural elements: (1) slickensides, which are in cross-sectional view associated to (2) a thin zone of slickenside parallel oriented particles, (3) gouge, (4) calcite and celestite veins and (5) scaly clay. We interprete the thin zones as tectnoic shear zones probably with milimetric offset, eventhough clear offset markers are absent. The lack of trans-granular microcraks indicates other deformation mechanisms along with cataclasis. We discuss processes of localization during incipient faulting in mudrocks at about 1.5 km depth, episodic fluid flow and resealing, and the formation of slickensided surfaces in deformed mudstones.

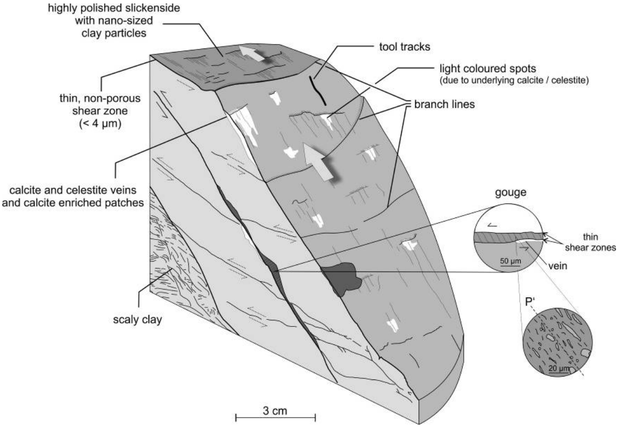

Figure 1. Generic model of faulted Opalinus Clay

The cap rocks sealing the reservoir in the Węglówka oil field, Sub-Silesian Unit, Polish Outer Carpathians – petrographical approach

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The Węglówka Oil Field, located in eastern part of the Outer Carpathians, is one of the most important areas where hydrocarbon is exploited. An anticline originated from thrusting and deformed by two thrust faults there is the structural trap. Oil production is from the Lower Cretaceous sandstones. The cap rocks in the field are the Upper Cretaceous Węglówka Marls (up to 300 m thick). The present work is to focus on the characteristics of these rocks to use it as analog in the prediction of seal capacity. The marls outcropping in the Węglówka appear as monolithic sequence composed of interbedding red and green varieties, which occur in medium and up to 2 meters thick beds, are nonarenaceous, soft, and abounding in burrows. The grain size of the marls corresponds to clayey and silty (<20%) fractions, whilst the content of sand is negligible (<1%). The XRD studies evidence that the marls contain on the average 54% clay (mostly illite-smectite), 28% calcite, and 16% quartz (mostly nanoquartz). There occurs up to 3% feldspars and, in the red variety about 3% hematite. The XRD patterns of <0.2 mm carbonate free particle size fractions in homoionic-saturated states are similar to those typical of low-smectitic random illite-smectite referred to as about 40% illite in I-S. The structural formulae have dioctahedral composition with similar octahedral Mg content and relatively high Fe^{3+} content. As revealed by the standard and high resolution petrographic analyses (FESEM/BS/CCI), the marls have wackstone texture, and are composed of coccolith fragments, and clay with nanoquartz, which serve as contact and pore-filling cements. These rocks are classified as dirty chalk. The effective seal rocks properties of the Węglówka Marls, indicated by the specific surface area and the pore size distribution calculated by N_2 Gas Adsorption, is postulated to result from a combination of: (1) origin of components (minute bioclasts and swelling clay originated from alteration of dispersed volcanic glass shards); (2) oxygenated sedimentary environment (burrowing producing sediments churned and homogenized); (2) tectonic-induced clogging of pore space (feathery clay wrapped around micarb).

Funding provided by the Grant no 11.11.140.319 of the AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection.

Evolution of pore space in organic-rich mudrocks from the Hilsmulde, Germany – studying the influence of thermal maturity on porosity in organic particles and the mineral matrix using FIB-SEM microscopy

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The goal of this study is to better understand the pore space distribution and evolution with increasing thermal maturity in potential shalegas plays. The samples investigated are Mid Jurassic Posidonia shales with increasing maturity ranging from Ro of 0.53 to 1.45 (Jochum et al., 1995 Ore Geol. Rev. 9:363-370). The method used was Focussed Ion Beam (FIB) microscopy coupled with SEM & EDX. A rock volume of 20 µm*10 µm*10 µm with a voxel size of 40 nm*40 nm*25 nm was investigated. The Secondary Electron (SE) images allowed differentiation of the porespace from organic matter and the mineral matrix based on surface properties of each slice. In addition, based on electron density differences in Backscattered Electron (BSE) images mineral groups such as silicates, carbonates and sulfides can be separated. EDX mapping of each slice allowed differentiation between minerals with similar electron densities such as silicates, carbonates, and oxides-phosphates-sulfides. Subsequent 3D modelling was performed using the Avizo software package and porosity measurements were compared with µCT and other porosity measurements.

The results indicate that with decreasing pore diameter the number of pores increases, regardless of the maturity of the samples. However, in the sample with the highest thermal maturity the porespace inside the organic matter increases significantly. In addition to reconstruct the pore space, the axis connectivity between the pores was determined, showing little to no axis connectivity between the axes. The size distribution as well as the axis connectivity will be applied to C-org and all differentiable minerals. From XRD the following minerals were identified: $2M_1$ illite, $1M_d$ illite-smectite, kaolinite, calcite, quartz, dolomite, ankerite, and pyrite with minor variation between the different thermal grades. The project outcome will include 3D models of the pores in the organic matter and the mineral matrix allowing modelling the effects of thermal maturation under natural pressure-temperature regimes.

Effects of diagenesis and fluid interactions on the properties of potential gas shales

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Shale gas potential mainly depends on the amount of gas in place and the fraccability of the gas shale. The fraccability of the shale is affected by the mineralogy of the rock, which is in turn controlled by the initial depositional environment and subsequent diagenetic processes. Diagenetic reactions in a rock formation, among others, affected by fluid flow and chemical interaction with the bounding formations. This study addresses the chemical interaction of the shale formations with the underlying carbonate rocks by fluid flow and possibly diffusion, and the effect that has on the shale mineralogy. We studied the Geverik Member and the limestone formation underneath, which are both Carboniferous. The limestone is fractured and locally carstified, indicating a high potential for fluid flow. Fractures connecting with the overlying shale can facilitate chemical interactions between the rocks. This might lead to alteration of the shale, involving precipitation/ dissolution reactions and possibly alteration of the clay minerals. Samples with increasing distance to the carbonate-shale boundary are studied to assess the differences in mineralogy. The chemical variations are identified using ICP measurements, while detailed clay fraction XRD measurements provide insight in clay mineral alterations as a function of depth. Microscopic analyses including SEM are performed to distinguish primary and secondary carbonate occurrence. To assess the geochemical interaction processes, an understanding of the primary depositional environment and the burial history is of great importance. To put our results in a regional context different locations are studied. To get an perspective on gas shales in general, the Geverik shales are compared to another Dutch organic-rich shale, the Posidonia Shale Formation (Jurassic). The study aims at identifying the processes affecting the shale mineralogy providing insight in the fraccability and therefore shale gas potential.

Influence of palaeoenvironment and palaeogeography on source rock potential and theoretical gas storage capacity of roof shales (drilling KB174, Hechtel-Hoef, Campine Basin, Belgium)

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Organic-rich shale deposits rich can be regarded as source and reservoir rocks for natural gas. Present-day research mainly focus on marine black shales, while other organic rich deposits are mostly overlooked, for instance shales in coal sequences. This study presents a re-evaluation of Rock-Eval data from 47 roof shale samples of the KB174 drilling (GSB 047E0196, Hechtel-Hoef) in the Campine Basin (Belgium) in terms of TOC (Total Organic Carbon) and S2 (amount of hydrocarbons released during pyrolysis). The averages are respectively 3.6% and 7.93 mg/g and show a good source rock potential (Vandewijngaerde *et al.*, 2013). These values differ when different palaeoenvironments (Paproth *et al.*, 1996) are taken into account. The average TOC values for palaeoenvironment A, B and C, ranging respectively from least to most marine influenced in the continental realm, measure 4.19% (A), 2.53% (B) and 3.69% (C). Averages for S2 are 9.47 mg/g (A), 5.53 mg/g (B) and 7.46 mg/g (C). The average TOC and S2 also differ for Westphalian A (6.37% and 13.14 mg/g) and Westphalian B (2.42% and 5.72 mg/g). Nonetheless, a regression trend line analysis of the TOC vs. S2 plots indicates that there are no significant differences in kerogen type. In other words, the differences in source rock potential are not due to the organic content of the sediment, but because of its potential to deposit and preserve organic matter, resulting in a higher TOC content. A petrophysical analysis is conducted to study whether palaeoenvironment and palaeogeography affects storage capacity. Natural gas can be stored as free gas in the pore spaces or as sorbed gas on the surface of clay or organic particles. Porosity is measured by means of low-pressure sorption with CO_2 and N_2, helium pycnometry and mercury injection porosimetry (MIP). High-pressure methane sorption determines the sorption capacity.

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Mineralogical changes in organic-rich Posidonia shale comparing natural with experimental maturation

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Typically the diagenesis of clay minerals and organic matter in shales are studied independently of each other. Here, we present the results of an experimental study that focused on the clay-organic interaction to understand the dissolution and precipitation processes of minerals as a function of thermal maturity. Three core samples of Posidonia shales (Hils Syncline, Germany) with different natural thermal maturity (WIC 0.53% $R_{o,}$ DOH 0.73% R_o, HAD 1.45% R_o) [1] were reacted in experimental aliquots. These were enclosed in gold capsules at 300 °C & 120 bars for 27 days in 0.3 M KCl (rock/fluid ratio 1:5) based on published smectite illitisation kinetic experiments[2]. The educts and products were analyzed by TEM and XRD. The clay minerals present in the educts were kaolinite, 2M1 illite and 1Md illite/smectite, whereas chlorite was only present in WIC. Main non-clay minerals were quartz, albite, calcite, dolomite and ankerite. The DOH sample, with moderate thermal maturity, had a high content of ankerite and dolomite.

In all experiments 1. kaolinite disappeared, 2. quartz and carbonates reduced, and 3. 2M1 illite decreased relative to the 1Md, demonstrated by the relative changes in peak intensities and the higher occurrence of lath shaped 1Md crystals observed by TEM. The calculated smectite content[3] in the 1Md increases in the products by up to 5%. New formation of sanidine was recorded in all samples; trioctahedral smectite was detected in the DOH sample, together with a lower neoformed sanidine content.

We concluded that the dissolution of kaolinite and quartz in a solution of KCl supplies the necessary cations to precipitate sanidine. Furthermore, the higher content of Mg in the mineral educts of DOH resulted in precipitation of trioctahedral smectite. The increase of smectite in 1Md phases confirms some neoformation, but the overall high illite content shows a mature illitisation. This is contrary to expectations of illitisation processes during published thermal maturity experiments[2]. Possible explanations: 1. duration of the experiment, 2. concentration of the KCl, 3. the highly illitic starting material.

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Interaction of drilling fluids with clay minerals of northern North Sea at reservoir conditions

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Manifestations of formation damage occurring at reservoir conditions in rocks of the northern North Sea were studied. Reservoir conditions were estimated as high pressure and high temperature and the period of testing in the laboratory was approaching actual duration of field operations.

Clear, solids-free drilling and completion fluid was used in one of examples. High-density formate brine-base mud systems were used as drill-in and completion fluids for deep high-temperature wells. These fluids are supposed to minimize reservoir damage and satisfy environmental requirements.

This paper describes caesium/potassium formate high density fluid interaction with reservoir formations at high-temperature high-pressure (HTHP) reservoir conditions. It was shown that the formation containing small amount of kaolinite and illite was detrimentally affected by the applied non-buffered Cs/K formate fluid and the laboratory measurements proved that there had been a significant decrease in permeability. When the same fluid was used along with the buffer the resulting permeability was noticeably increased. Detailed study on after test core samples using SEM/EDS analysis and imaging micro-CT scanning suggested a deep damaging effect of non-buffered formate fluid on the clays. The paper shows the images of before and after test core samples and describes possible mechanisms involved.

The nature and origin of the clay minerals in North Sea reservoir sandstones and their influence on formation damage

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The most common clay minerals in the hydrocarbon reservoir sandstones of the North Sea are well-crystallized kaolinite, mainly occurring as pore-filling vermiform and booklet-like aggregates, illitic clays usually in the form of pore-filling networks of thin lath-like, filamentous or hairy particles, and chlorite, most commonly found as pore-lining aggregatesof interlocking, well-developed, bladed crystals. All these clay minerals are authigenic (diagenetic) in origin.

The crystallization of kaolinite in these sandstones has been attributed to a variety of stages in the paragenetic sequence, particularly in relation to authigenic formation of calcite and quartz. However, most evidence suggests that vermiform kaolinite is a product of early diagenesis at temperatures ranging from surface to 40 degrees C, either before or contemporaneously with carbonate cementation and before the formation of quartz overgrowths.

The illitic clay in these sandstones is usually described in terms of two discrete phases, namely illite itself and mixed-layer illite-smectite (I/S). In all probablility, however, only one illitic phase exists in these sandstones and the mixed-layer material in reality consists only of very thin illite (<5 nm in thickness).Illite is also considered to exist in both pore-filling and pore-lining modes, with the latter forming at low temperatures very early in the paragenetic sequence, perhaps even in equilibrium with depositional pore waters. In contrast, pore filling illite is thought to have formed at higher temperatures, in excess of 100 degrees C, following deeper burial. Evidence is presented to show that pore-lining illite is sometimes an artefact of the drying procedure of sandstone samples prior to examination by SEM or optical microscopy.

Both kaolinite and illite are involved in formation damage of the rervoir sandstones through dispersion, migration and pore blockage but there is little evidence that chlorite also behaves in this way.

Cation exchange capacity and water content of opal in sedimentary basins: example from the Monterey Formation, California

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Surface characteristics of sedimentary opal A and CT were investigated for a large collection of samples from the Monterey Formation, California, based on the bulk rock mineral and chemical analysis, cation exchange capacity (CEC) and water content. Two approaches were used: (1) modeling bulk CEC and adsorbed water content for the entire data set using the contents of opal and clay minerals measured by XRD, and (2), correcting the chemical composition and CEC of the most pure opal samples for the mineral impurities quantified by XRD.

Modeling indicates that the bulk rock data can be best explained by mixing an illite-smectite (CEC=59 meq/100 g, 7-8% H_2O), consistent with the XRD characteristics of the clay fraction, with opal-A (8 meq/100 g, 3.4% H_2O), or opal-CT (13 meq/100 g, 3.7% H_2O).

Correcting the chemical composition of the most pure opal samples leaves a large excess of cations (Al, Fe, Na, K, Ca, and Mg). Iron is suspect to form traces of separate (oxy-)hydroxide phases, not detected by XRD, while Al for Si substitution in the opal structure produced local negative charge, which was compensated by Na, K, Ca, and Mg exchange cations. A perfect balance of positive and negative charges is observed if the clay admixture in pure opals has the composition of montmorillonite. The concentration of heterogeneous impurities in silica network in opal leads to smectite formation on or within the diatom frustules. These dispersed smectite particles, perhaps monolayers, can be missed during the bulk rock mineral quantification. The recalculated CEC of the opal, assuming the occurrence of dispersed smectite particles, varies from 3 to 11 meq/100 g, which is slightly less than that evaluated by modeling all the rock samples in the set, and corresponds to ~ 10-50% of the total opal charge quantified by the degree of Al for Si substitution. The remaining charge of the opal structure represents non-exchangeable cations. As opposed to smectite, opal CEC may depend on the size of cation used for the CEC measurement.

Different fractions of water in the opal structure and opal surface properties affect wire-log measurements in diatomaceous hydrocarbon reservoirs. For opals in the Monterey Formation the content of water removable at 200 ºC can be modeled as a sum of a constant value and a function of CEC similar to the relationship that is typical for smectite. The combined system of a constant H_2O + variable H_2O in opal can potentially be applied for mineral modelling programs in wireline log formation evaluation.

Effects of clay particles on the formation of methane hydrates in aqueous solution

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Methane clathrates are crystalline inclusion compounds that form at low temperatures and/or high pressures when methane is trapped within host water cages. Methane hydrates occur in tundra regions and deep-ocean and sedimentary environments, and are currently under intense investigation as a major potential source of natural gas.

We have used neutron diffraction to compare methane hydrate formation in the absence and presence of clay particles of varying charge densities, under forcing conditions of 5 ^{o}C and 180 bar methane. In all cases methane is taken up by the water prior to the formation of crystalline hydrates, which then takes place over several hours. The data are consistent with multiple nucleation centres in the sample and rapid growth to a crystallite size of >200 Å. There is also evidence of hysteresis or “memory effects” in that once the initially formed hydrates have been melted hydrates form much more readily on re-cooling the sample. These experiments confirm the power of neutron scattering for these systems and provided new insight into the mechanisms and time-scales of hydrate formation.

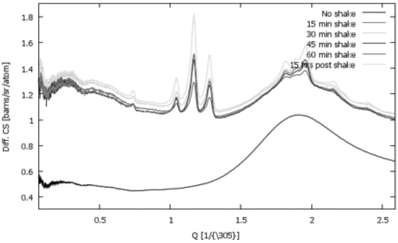

Figure 1. D_2O at 180 bar CH_4 and 5 °C (close up of hydrate Bragg peaks formation after shaking)

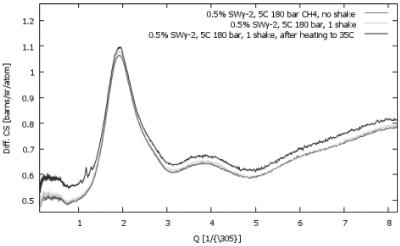

Figure 2. Swy-2 Smectite-2/D_2O at 180 bar CH_4

CO_2/clay interactions and the significance for geological storage of carbon dioxide

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For the characterization of CO_2 storage reservoirs a number of critical parameters need to be assessed, like storage capacity or injection rate, which is a straight-forward work flow based on existing experience in the oil and gas industry. Added complexity is in the identification of (potential) leakage pathways along wellbores, faults/fractures or even capillary seal networks. Important aspects are mechanisms and rates of leakage.
Over the last few years we intensely worked on an improved understanding of the interaction of CO_2 with clay minerals, with a major focus on swelling clays, such as montmorillonite. It was found that for CO_2 storage and storage containment non-negligible physical effects result from clays in contact with CO_2 and water under pressure, temperature and stress conditions representative for geological reservoirs. Several cases where this interaction might become important are summarized in Figure 1. This contribution aims at summarizing these effects, increasing awareness and discussing the significance for the geological storage of CO_2.

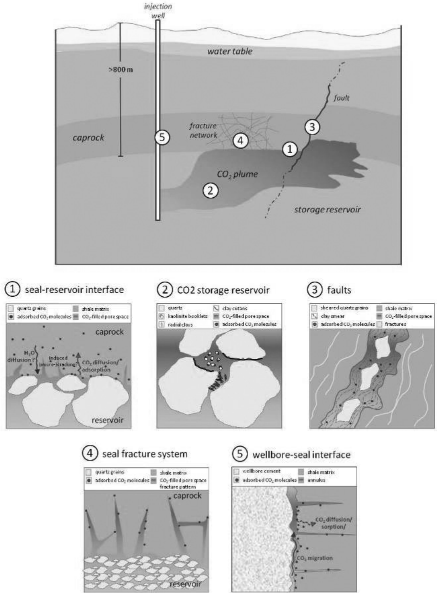

Figure 1. Different scenarios of CO2/clay interactions affecting reservoir performance or seal integrity.

Structural diagenesis of an Upper Carboniferous Tight Gas sandstone reservoir analogue

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Reservoir characterization of tight gas sandstones can be enhanced by integration of quantitative data from outcrop analogue studies. This study focuses on the holistic approach of structural diagenesis and presents the heterogeneity exposed in the Piesberg quarry near Osnabrueck. This reservoir analogue consists of fluvial sandstone cycles (Westphalian D), made up of coarse- to fine-grained strongly cemented sandstones, fining upwards into siltstone, shales and coal seams.

Primary pore space is substantially occluded by a pseudomatrix, consisting of shale-, mudstone and clay rip-up fragments, resulting in low porosities (<10%) and low permeabilities (<0.01 mD). Further porosity reduction was caused by quartz and illite and minor chlorite cementation. The remaining porosity is secondary and resulted mostly from carbonate dissolution. Around faults dissolution is higher and the porosities can increase up to 25%. Uniaxial strengths of more than 180 MPa normal to, and approximately 50 MPa parallel to bedding were measured on sandstone samples. Mechanical rock strength measurements also reveal a weakening of rocks around faults, resulting in decreased rock strength of 35 MPa. Shale and coal beds are smeared into faults, which may result in reservoir compartmentalization. Terrestrial laser scanning enabled analyzing joints in a 50 x 50 m section of the quarry wall and allowed characterizing the lithology as well as quantification of bedding and fracture orientations. Dominant sub-orthogonal joint sets were revealed, which are aligned parallel to normal faults. Fracture patterns become more heterogeneous around faults. Fractures and fault planes are cemented with quartz around faults, indicating localized mass transport.

The Piesberg quarry is identified as a suitable outcrop reservoir analogue for the Upper Carboniferous tight gas fields of the Lower Saxony Basin, in terms of size, facies, structure and diagenesis. A predictive model for the distribution of carbonate cements, carbonate dissolution porosity and related porosity-permeability variations in tight sandstones is currently being established. Results will allow quantification of the effect of structural diagenesis on gas-in-place versus recoverable volumes. Model predictions will also provide relevant information for well-placement and reservoir stimulation methods for tight gas sandstone reservoirs in the region.

Definition of shale minerals in reservoir area using geochemical sampling

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Chemical changes of shale have been a source of trouble for petroleum engineers for many years. Although swelling as chemical changes in shale may cause serious instability, but other chemical changes may exist in shales, especially if they are present in reservoir area. Geochemical sampling of a gas well performed in a wellbore, southernIran. Since enough core samples in reservoir area was not available and cutting samples were not reliable enough, geochemical samples were used to identify shale minerals in openhole section. The data of North Sea area of Cretaceous age were used as control tests in a simulated model to define the accuracy and uncertainty of proposed model. The results were satisfactory enough and confirmed the validity of suggested method. Final results revealed that a considerable percentage of the shale inter-bed contained expandable shale mineral and some strategies proposed and modified for better production of the whole gas reservoir.

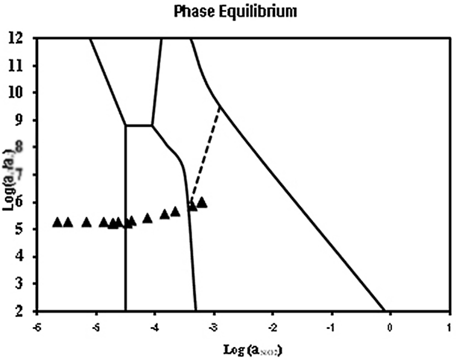

Figure 1. Phase diagram of 7737 ft depth. Solid lines define the margins between the phases and data points show the experimental results.

Identification of clay minerals in the Cheleken reservoir series in South Caspian and appropriate drilling mud selection

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Siliciclastic sediments of the Cheleken reservoir series (lower to middle Pliocene) are exposed along the northern flank of the Albourz Mountain range in Mazandaran and Golestan provinces of Iran. The main goal of this research was to identify clay minerals in the above mentioned sediments. Identification of the clay types has a significant effect on selection of drilling mud type. Therefore 23 representative samples were collected from three regions including Neka, southern Ghaem-Shahr and Alamdeh. A core from a depth of 3720 m in the Caspian Sea was also examined.

Microscopic studies showed that these sediments contain quartz, calcite, plagioclase (albite and anorthite) and minor amount of opaque minerals. In some thin sections minor amounts of illite were recognized. To confirm identification of this and other clay minerals X-ray diffraction (XRD) was used while specific treatments should be implemented prior to XRD analysis for determination of clay types. Illite and kaolinite were the main clay minerals, with montmorillonite and chlorite traces.

For drilling mud selection criteria, appropriate additives should be applied because of clay minerals. As montmorillonite makes a very low percentage of the shale section, drilling mud selection is not a very serious dilemma and regular mud with small amount of potassium salt would be satisfactory. Considering economical concerns and availability of suitable additives in local region may also lead to use sodium chloride during drilling with a more experienced driller and speed up drilling through the shaly carbonates.

Clay-mineral composition of black shales from the Dniepr-Donets Basin (Ukraine)

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The amount and type of clay minerals in sedimentary rocks is primarily controlled by the prevailing tectonic setting and compositional features of the clastic influx from the hinterland, often showing high lateral variability within a basin. Besides these obvious influencing factors, a second major aspect is the vertical evolution of clay mineral distribution caused by thermal maturation and diagenetic reactions. Within the frame of this study, both lateral and vertical compositional changes were investigated on Late Devonian to Carboniferous black shales from the Dniepr Donets Basin, a Late Devonian rift basin with syn-rift sediments up to 4 km thickness and post-rift sediments in excess of 15 km. On the base of a numerical modelling study of the thermal evolution of the Dniepr-Donets Basin (Shymanovskyy et al. 2004) the attempt was made to correlate the changes in composition and crystal structure of clay minerals with the thermal history and maturation history of organic matter in black shales. The percentage of illite present in illite-smectite-mixed layer clays was used as an indicator for the reconstruction of the thermal evolution of the basin. Expandable clay minerals are preserved at a depth of more than 5 km as a result of low Mesozoic heat flow. XRD-analyses on core samples of selected profiles show the varying amounts of chlorite, kaolinite, illite, smectite and illite-smectite-mixed layer minerals. A discrete mineralogical composition in contrast to underlying, Lower Visean shales was observed for the organic rich Upper Visean “Rudov Beds”. Relatively low kaolinite contents and a higher abundance of illite and illite-smectite-mixed layer minerals, the presence of apatite and partly high silica contents stay in clear contrast to the surrounding rocks. Within the so-called Srebnen Depression, a vast syncline surrounded by a reef belt, clay rich rocks prevail along the northern reef margin as well as in the NW part, whereas a quartz-dominated siliceous facies occurs in the SE part. The portion of brittle mineral phases is an important factor for hydrocarbon production.

Crystal structure of clay minerals

The phyllomanganates – crystal structure of a large family

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Manganese oxides are ubiquitous minerals in nature where they play a major role in the trace metal partitioning due to redox properties and high cation exchange capacity, enhanced by a high specific surface area. The main member of the phyllomanganate family, called birnessite, is a lamellar manganese oxide made of sheets of edge-sharing Mn octahedra. Hydrated cations located in the interlayer region, with an ordered or random distribution, insure structure cohesion and compensation for a layer charge deficit arising from the coexistence of heterovalent Mn cations and/or the presence of octahedral vacancies. In addition, both the nature of the interlayer cation and the presence or absence of heterovalent Mn induce versatility in the layer stacking modes that can easily coexist within individual crystals, leading to a potentially high occurrence of structural defects such as random or defined stacking faults, and polytype interstratification.

Because of these crystal-chemical properties, responsible for its unique behaviour, natural birnessite focuses attention for its potential use in the rehabilitation of contaminated soils or water resources. However, the highly defective structure of natural birnessite can prevent or at least considerably reduce the understanding of adsorption mechanisms at the molecular level. A great effort has thus been devoted to unravelling the detailed structure of synthetic analogous polytypic variants. Coupling chemical analyses, X-ray and electron diffraction and EXAFS spectroscopy has allowed demonstrating the direct link between the crystal structure and the origin of the layer charge. In addition, it was shown that the charge origin is a key parameter having direct consequences on the redox properties of birnessite, on its cation exchange and adsorption capability, as well as on its structural stability as a function of the pH, thus impacting directly its long-term efficiency in the retention of soil contaminants.

Structure of nanocrystalline calcium silicate hydrates

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Nanocrystalline calcium silicate hydrate (C-S-H) is the main hydration product and the main binding phase in many types of cement where it controls main physical and chemical properties. These properties depend on C-S-H calcium to silicon atomic ratio (Ca/Si), which is commonly described as ranging between 0.6 and 2.3. This means that C-S-H structure dictates cement macroscopic properties. As a consequence, a sound description of its crystal-chemistry is required to understand (and thus predict) cement properties. However, despites decades of study, its crystal structure is still a matter of debate. Depending on the authors and on the Ca/Si ratio, the structure is described similar to one or more of the following minerals: tobermorite, jennite (two layered minerals) and possibly portlandite. Such ambiguity largely results from its X-ray diffraction pattern, which exhibits only a few weak and mostly asymmetrical diffraction maxima and thus cannot be refined using classical methods. By using a specific formalism developed for the analysis of X-ray diffraction patterns, previously applied to phyllosilicates and phyllomanganates, it is here proposed that C-S-H can be described as a lamellar structure similar to nanocrystalline and turbostratic tobermorite, turbostratism meaning that there is the systematic presence, between adjacent layers, of a random rotation about the normal to the layers and/or a random translation in the layers plane. Layers are built of calcium polyhedra and silicon chains and are separated by a hydrated interlayer space. This model was validated by using complementary methods (including transmission electron microscopy, and different methods taking advantage of synchrotron light source such as EXAFS). It is proposed that the evolution of C-S-H structure as a function of Ca/Si can be described by interstratification of two different types of layers having Ca/Si ratios of 0.6 and 1.25, plus $Ca(OH)_2$ at higher ratios.

Structure of phyllosilicates as a challenge for functional nanostructures

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The relationship between the structure of phyllosilicate and structure of composite phyllosilicate/conducting polyaniline (PANI) and phyllosilicate/graphene has been investigated step by step during the preparation process, including the high pressure and high temperature treatment. Structural study, which included combination of x-ray diffraction, IR and Raman spectroscopy with molecular modeling, enabled an understanding of high conductivity of the resulting nanocomposites. The structure and unique properties of phyllosilicates are generally a great challenge for the construction of various functional nanostructures, nevertheless this work is focused on the effect of layered structure on the alignment of conducting polymer chains in the interlayer space of phyllosilicates [1- 4]. This effect results in highly electrically conductive ceramic material, prepared either in the form of pressed pellets or in the form of thin films. Due to the layered structure and proper layer charge of montmorillonite (MMT), PANI chains are well aligned in the monolayer arrangement in the interlayer space of MMT. Fortunately, this arrangement of PANI layers is not destroyed by a high temperature treatment, thanks to the character of high temperature phase transition of montmorillonite into cristobalite and mullite. Therefore, the texture and anisotropy in conductivity remains preserved in the resulting aluminosilicate/graphene nanocomposite. The composite aluminosilicate/graphene shows a much higher conductivity than any composite with graphene, does not matter whether in organic or inorganic matrix. Simple fabrication method of aluminosilicate/graphene tablets is very promising for the manufacturing of the electrically conductive and tough ceramic material, which can be exposed to corrosive environment as well as to high temperatures. Present results revealed the crucial effect of MMT layers on the nanostructure of PANI films, showing much higher conductivity than PANI films grown on other substrates.

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[3] J. Tokarský et al: *Appl. Clay Science 80-81 (2013) 126-132*
[4] L. Kulhankova et al: *Submitted in Thin solid films (after revision)*
[5] P. Čapková et al: *Submitted in J. of European Ceramic Soc. (after revision)*

Comparison of different force fields by coupling molecular simulations of organo-clays with X-ray diffraction data

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Due to a large variability of different force fields for (bio-)organic materials it is important to understand which set of parameters is the most suitable for molecular modeling of the structure and properties of intercalated organic species in clays. The intercalation of ethylene glycol (EG) in smectites provides stable interlayer complexes with relatively constant basal spacing. These structures are also relatively well characterized experimentally, providing their molecular contents of EG and water. Therefore, this system is used here as a test model.

The molecular dynamics simulations were performed for two models of montmorillonite with substantially diferent layer charge: SWy-1 and SAz-1. Their structural models were built on the basis of pyrophyllite crystal structure, with substitution of particular atoms. The interatomic interactions in the smectites were described with CLAYFF and INTERFACE force fields. The interatomic interactions for EG molecules were described by the parameters of one of the organic force fields: AMBER, GLYCAM06, OPLS-aa, CGenFF and CVFF. Recent studies showed that SPC/E water model most efficiently describes the distribution of interlayer water in smectites, therefore only these parameters were used for H_2O in the simulations.

A set of systems with different contents of water and EG close to those of Reynolds (1965) was covered: 1.7 EG and 0.8 H_2O per half unit cell. For every structure, the atomic density distributions of the interlayer species perpendicular to the layer plane were calculated. Then X-ray diffractograms were calculated for these structures, using the Sybilla code (Chevron proprietary). The values of T_{mean}, σ^* and *delta d*-spacing were optimized.

The results show very large discrepancies in obtained structures and basal spacings for different layer charges as well as for different force fields. There is an intuitive tendency that for larger Lennard-Jones parameter σ for the EG atoms, the corresponding basal spacing will also be larger. In some cases, however, in spite of the well reproduced basal spacings, the corresponding diffractogram only poorly agreed with experimental data. The best results were found for the combinations of INTERFACE/GLYCAM06 and CLAYFF/AMBER force fields. On the other hand, CGenFF, being very succesfull in other applications, results in theoretical diffractograms very different from the experimental ones, and should not be used to study interlayer species in smectites.

Modelling the diffraction pattern of lamellar materials – structure, microstructure, and faulting

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Clays show unique promise in many fields of applied materials science. The possibility of ion substitution in both the layers and interlayers, in addition to the potential for engineering the layer sequences themselves, can lead to a huge variety of compounds, each with unique and potentially novel properties. Unfortunately, the lamellar character of these systems introduces an extra level of complexity into the powder diffraction patterns. This complexity is such that generally only qualitative microstructure parameters are extracted from powder diffraction data of clays. The analysis is in fact mostly limited to a pattern simulation [1] (aimed at reproducing the effects of stacking disorder) or to the analysis of the breadth and location of basal reflections [2]. Meaningful refinements, which yield both quantitative information on the structure, microstructure, and layer disorder, are not common-place [3].

Here we outline a new 2D - 3D Rietveld-like approach to model the powder diffraction data of lamellar materials, including disordered clay systems. The approach embeds physically meaningful descriptions of the instrument and microstructure [4] and includes a Markov-chain stacking algorithm [5]. This approach allows for the refinement of the most probable faulting structure, as well as the shape and size distribution of the crystalline domains in the sample. Practical applications are shown.

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Identification and quantification of complex soil clay mineralogy by using X-ray diffraction profile modelling

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Identification and quantification of soil clay minerals in soils are delicate issues due to the complexity of the clay mineralogy encountered in soil environments. This complexity is mainly due to the important chemical and structural heterogeneity of clay minerals found in soils. Indeed, several types of clay minerals (kaolinite, chlorite, smectite, illite, mica, and others) commonly coexist within a wide range of particle sizes (from ~50 nm to ~5 µm). In addition, the presence of mixed-layer minerals (MLMs) in which different types of clay layers coexist in the same crystal is most often observed in these environments.

By performed X-ray diffraction (XRD) analysis on oriented sample of the <2 µm fraction, the classical identification is based on the different behaviours of the clay crystal structures submitted to various treatments. In addition, decomposition of the 001 reflections has been repeatedly applied to improve the discrimination between MLMs and discrete clays from soils. However, the identification derived from such an approach is limited to the less defective clays, which exhibit the most evident diffraction maxima (Hubert et al. 2009) whereas the nature and proportion of the most defective and reactive clay structures remain to be determined.

The XRD profile modelling approach applied on various sub-fractions of the bulk <2 µm fraction (<0.05, 0.05-0.1, 0.1-0.2 and 0.2-2 µm) allows revealing the complexity of soil clay mineralogy (Hubert et al., 2012). The results obtained from different soils (Luvisol, Cambisol, Alocrisol, Planosol) show that the finest and most reactive particles are not visible on the experimental XRD profile of the bulk <2 µm fraction whereas their relative proportion range from about a 20 to 65% of the sample mass. The finest sub-fractions are mainly composed by MLMs with low coherent scattering domain size and MLMs are also the dominant clays of the bulk <2 µm fraction. Based on the relative contribution and the crystal structure of the different clay phases, the different pedogenesis can be assessed. However, although highly complex in appearance, numerous similarities can be noticed between the compositions of MLMs from various soil environments.

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Aluminoceladonites – crystal-chemical peculiarities, identification and occurrence

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Aluminoceladonite is a potassium dioctahedral mica having very low tetrahedral Al for Si substitution or none, and high contents of octahedral Mg cations, with the idealized crystal-chemical formula $KAl(Mg, Fe)Si_4O_{10}(OH)_2$. Aluminoceladonites normally occur as *trans*-vacant 1*M* polytypes and have been found mostly as products of recrystallization of volcanic glass by hydrothermal activity or under the action of highly-mineralized solutions in evaporitic basins.

In sedimentary rocks, Al-rich K-dioctahedral 1*M* and 1*M*d micas form a virtually continuous series from Mg, Fe-free illite via Mg-rich illite to aluminoceladonite. The actual abundance of aluminoceladonites, however, may be underestimated, as they may be confused with illites, all the more that the former can occur as interlayer-deficient varieties with up to 20% expandable layers. Our purpose has been to develop techniques and formulate criteria for reliable identification of aluminoceladonites, based on the analysis of their structural and crystal-chemical peculiarities obtained using a combination of experimental data (XRD, FTIR, and DTG) and structure modeling.

Specific features in powder XRD patterns and FTIR spectra of aluminoceladonite, as well as their dehydroxylation behaviour will be treated in detail in order to demonstrate the differences from the respective characteristics of illites. These distinctive features include, among others, reduced *csinß* and *b* parameters; the presence of the MgOHMg band in FTIR spectra; evidence of partial rehydroxylation during heating-cooling cycles in the DTG curves. Crystal-chemical factors will be analyzed that are responsible for these peculiarities.

In contrast to 1*M* mica varieties, high-temperature K-dioctahedral $2M_1$ and 3*T* micas only form a series between muscovite and phengite. Samples with cation compositions intermediate between phengite and aluminoceladonite have not been found in nature and were only synthesized under extremely high temperature and pressure. Possible reasons for this difference in the composition variation range between low- and high-temperature dioctahedral micas will be discussed.

High temperature studies on zinnwaldite – structural changes up to 800 °C

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Zinnwaldite $K(Li,Fe^{II},Fe^{III},Al,\Diamond)_3(AlSi_3)O_{10}(OH,F)_2$ (◊ vacancy) is a local lithium-iron mica and the only economic resource of Lithium in Germany. Production processes are based on calcination with alkaline additives [1-2] or acidic leaching procedures [3]. Understanding the thermal behavior of the mineral gives the opportunity to optimize calcination and other extraction processes. Publications regarding to the specific subject of thermal transformation in trioctahedral mica with high content of ferrous iron and fluorine are rare. Rancourt et al. studied the oxidation kinetics of Biotite samples with Mössbauer spectroscopy [4]. Muller et al. and Drits et al. published detailed descriptions and explanations on structural changes in dioctahedral micas with Fe^{3+} and Mg in the octahedral layer [5-7] .Thus the influences of features like the high fluorine content on structural changes are still not well understood. In this work various spectroscopic methods (FT-IR, MAS-NMR and Mössbauer), thermal analysis, SEM-EDX and powder x-ray diffraction were applied to investigate structural and chemical alterations step by step with increasing temperature. Comparisons between samples, prepared under oxidizing and nonoxidizing atmosphere, help differentiate effects of temperature and of oxidation, respectively. Changes in the oxidation state of iron, in the coordination of aluminum and the occupation of the octahedral positions could be distinguished.

A dominant factor is the oxidation of the ferrous iron in the octahedral layer, which is coordinated by F^-, OH^- and O^{2-}. The enforced charge-balancing has a major impact on structural changes.

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Characterization of iron sites in a fine grained illite

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Sorption to mineral surfaces is a major process controlling the concentration and mobility of radionuclides in natural environment. Therefore it is essential to understand the redox behaviour especially of clay minerals like illite or smectites, which strongly depends on the iron distribution and oxidation state within their structure. In this study the occupancy of possible iron sites in the structure of the very fine grained and relatively iron-rich Illite du Puy was investigated. Furthermore the mineralogical characterization of the fraction <0.2 µm gave hints for two additional sources for iron: a small amount of a illite/smectite mixed layer phase assoziated with the illite and a iron-oxide phase, which is still present in the fraction <0.2 µm. Besides a strong doublet at 0.35 mm/s and 0.7 mm/s of octahedrally coordinated Fe^{3+}, Mössbauer spectra additionally show a small and narrow peak at 2.5 mm/s which is attributed to Fe^{2+} also in an octahedral environment. This coordination of the Fe^{3+} was also visible in infrared spectra (Fig. 1). The iron was not only located in Fe-clusters (Fe-Fe-OH deformation band at 825 cm^{-1}), also Al-Fe-OH (874 cm^{-1}) and Fe-Mg-OH groups (765 cm^{-1}) were observed, showing a complex distribution of iron in the ocathedral sheet of this illite.

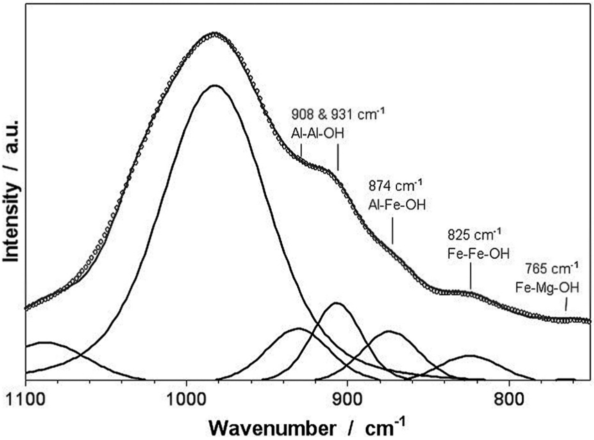

Figure 1. FTIR spectrum showing the OH-bending region of illite, with several bands which can be attributed to Fe-vibrations

Crystal-chemical controls on smectite hydration

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Swelling clay minerals such as smectites are ubiquitous at the Earth surface and possess major hydration ability and contaminant uptake/retention capacity. As a consequence smectites exert a pivotal influence on elemental transfers in surficial environments. These properties are especially relevant also when smectites are used as sealant in engineered or geological barriers for waste disposal facilities. As interlayer H_2O molecules account for more than 80% of smectite water in undersaturated conditions, characterization of H_2O organization and dynamics in smectites interlayers is essential to determining the geometrical and dynamical properties of clay barriers for waste disposal and to predicting the mobility of contaminant whose principal vector is water.

Within this general framework, the main goal of the present talk is to review the influence of structural parameters such as the amount and location of layer charge deficit and the chemical composition (and more especially the presence of structural fluorine/hydroxyl) on smectite hydration properties. A set of samples covering the whole compositional range of swelling phyllosilicates has thus been synthesized and characterized chemically and structurally. Special attention was paid to determining the amount (water vapor sorption isotherms) and the distribution (X-ray diffraction) of interlayer water.

Molecular modeling allowed unraveling the origin of the contrasting behaviors observed experimentally and to determine the influence of the different crystal-chemical parameters on smectite hydration. This step is essential for the prediction of smectite reactivity in the environment from a limited number of crystal-chemical parameters.

Identification of the external surfaces structure of organo-clays an XPS and MD study

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Organo-clays have been proposed as selective sorption material for the use in wastewater treatment and barriers of waste deposits. The arrangement of the organic cations in the clay interlayer as a function of the applied amount of organic cations has been studied in detail (e.g., [1], [2]) in contrast to the modification of physicochemical properties of the external surfaces. As the character of the solid-solution interface is a crucial factor controlling transport processes of environmentally hazardous solutions through barriers, the effect of increasing loadings (up to 3.5 times of the CEC) of organic cations [hexadecylpyridinium- (HDPyCl) and hexadecyltrimethylammoniumchlorid (HDTMACl)] on the external clay surface has been investigated. X-ray photoelectronspectroscopy (XPS) combined with molecular dynamic (MD) simulations were used to deduce the resulting arrangements of organic cations on the external clay surfaces. Supplementary, changes of surface properties have been evaluated by surface charge and wettability analyses. MD simulations using the LAMMPS package [3] on organoclay-water slab models with a surface coverage range from 0.125 to 1.5 HDTMA$^+$ ions/A$_{uc}$ (unit cell area) were performed. Findings of XPS and MD confirm the formation of mono- to bilayers parallel or perpendicular to the clay surface with amount of cations applied. This was supported by an increase of surface charge with amount applied (-119 to +55 mmol$_c$/kg) and varying wettability (hydrophilic/hydrophobic). Results show different arrangement of organic cations on the surface compared to that proven for the interlayer. Our data thus demonstrate that the varying amount of organic cations on the external surfaces determine the properties of the clay-solution interaction, which will inevitably affect the transport behavior at the solid/liquid interface of the modified clays. Combined experimental and MD studies proved to be powerful tools in identifying the surface arrangement of organic cations and Cl$^-$/Na$^+$ counter ions on external the clay surfaces and improved knowledge in clay mineral surface characteristics.

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Interlayer Li^+ in dioctahedral smectites as probe for an improved structural characterization

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Dioctahedral smectites are characterized by a huge structural variety that results in different reaction behavior, e.g. with respect to hydration and charge reduction after heating of Li^+-saturated samples. Interlayer Li^+ was used as a probe to explore those differences for a set of montmorillonites extracted from bentonites of different provenance.

A series of layer charge reduced samples of each montmorillonite was prepared by heating Li^+-saturated samples up to 300 °C, which were characterized by a combination of established mineralogical methods and ^7Li magic-angle spinning nuclear magnetic resonance spectroscopy (MAS NMR).

Characterization of the montmorillonites with established mineralogical methods revealed cation exchange capacities between 81 and 122 cmol/kg; zero to 70% of trans-vacant octahedral sheets; 0.03 to 0.30 mol/$O_{10}(OH)_2$ tetrahedral substitutions by Al^{3+} and 0.10 to 0.51 mol/$O_{10}(OH)_2$ octahedral substitutions by Fe^{3+}; as well as layer diameters between 70 and 200 nm.

The qualitative description of layer charge reduction and MAS NMR signals was consistent with previous reports [1, 2]. However, the influence of structural features was studied in more detail. Assessment of the analytical data resulted in the following main findings [3]: (1) The cation exchange capacity (CEC) of the Li^+-exchanged montmorillonites after heating to 300 °C reflected the remaining CEC at the edges of the particles and thus, the lateral size or aspect ratio of the 2:1 layers. (2) ^7Li MAS NMR revealed that hydration of interlayer Li^+ is, besides amount and type of isomorphic substitutions, strongly determined by the structure of the octahedral sheet in the dioctahedral 2:1 layers An axially symmetric chemical environment of the hydrated interlayer Li^+ with $h_{CS} = 0$ for the chemical shift anisotropy tensor was observed for more than 44% trans-vacant octahedral sheets.

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Intercalation of cationic polyelectrolytes into swollen vermiculites

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Vermiculites are layered aluminosilicates consisting of negatively charged plates neutralized by cations. The introduction of an organic ion such as n-butyl ammonium into vermiculites makes it possible to swell the vermiculite in water to layer spacings of up to 100 nm. If a water soluble polymer is incorporated into the swollen vermiculites the polymer can act as a bridging flocculant between the plates. The swelling of vermiculite by the branched cationic polyelectrolyte poly(ethyleneimine) (PEI) has been studied using both small angle neutron scattering (SANS) and direct measurement of the macroscopic swelling. The two methods showed good agreement indicating that the swelling is homogeneous in nature.

Intercalation into the vermiculite of all polymers was observed and interplatelet spacings of more than 250 Å were seen for the largest polymer samples as compared with 19 Å for the unswollen crystals. The swelling increased with increasing molecular weight but interlayer spacings were much lower than those seen at similar BAC concentrations in the absence of polymer. A decrease in swelling was also seen with increasing polymer concentration at fixed salt, with the exception of the largest polymer where the opposite effect was seen and the spacings *increased* as a function of polymer concentration. Previous studies on uncharged linear polymers showed an opposite effect with molecular weight in that the spacings was constant for large polymers but increased with a low molecular weight sample. That study observed decrease in swelling when the dimensions of the polymer corresponded roughly to the clay spacings and the assumption was then made that the smaller polymers are incapable of bridging the interplatelet gap and hence no reduction in spacing occurs. The results for the branched PEI systems here clearly contrast with that idea. The enhanced decrease in swelling with the low molecular weight PEI samples suggests that these are exerting the most force between the oppositely charged clay plates. However, the dimensions of these polymers are too small for an individual molecule to bridge the interlayer gaps at the BAC concentrations used and the nature of the interaction mechanism is therefore unclear.

A decrease in interlayer spacing with applied stress was seen for all the polymers and also in the absence of polymer

Rietveld refinement of structureal parameters of dioctahedral smectites

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X-ray powder diffraction (*XRD*) is one of the most common methods used for analysis of crystal structures. Unfortunately, almost all smectite minerals show turbostratic disorder. Such structural defects lead to strongly asymmetric peak broadening and can not be described by traditional Bragg peak profiles, precluding the application of the classic Rietveld method.

It was already proved that *BGMN* software can calculate turbostratic disorder features of the diffraction patterns using a supercell approach (*Ufer et al., 2004*). In this approach a standard cell was elongated in the c* direction and filled only by one single 2:1 layer. Such method makes the calculation of structure factors periodically in the a and b directions and aperiodically in the c direction and allows to model the asymmetric broadening reflections which are caused by turbostratic disorder. This model was applied successfully for phase quantification of smectites (*Ufer et al., 2008*), but the refinement of structural parameters has not yet been tried.

First, the Rietveld refinement of certain structure parameters and their relevance was tested by refining them from simulated patterns. These data contained three different series, each varying one of structure parameter (such as proportions of *trans*- or *cis*-vacant layers, iron content and layer charge). The refinement began with incorrect values of the structural parameters, but the atomic coordinates were kept fixed. Correlation problems have been observed between octahedral iron content and interlayer occupation.

Then, similar models (with varying atomic coordinates) were applied to experimental data. A series of dioctahedral smectites covering a broad range of composition and structure was chosen for testing the structural model and evaluating the application of this approach. The smectites were purified and characterized by *XRD*, chemical and thermal analysis methods. Conventional laboratory *XRD* powder patterns were obtained from the *Cu*-triethylenetetramine exchanged smectites avoiding the problems of unknown cation species and hydration stage in the interlayer (*Kaufhold et al., 2011)*. The iron content of the octahedral was constrained to the refined lattice parameter b_0 *(Heuser et al., 2013)*. The results of the refinements are discussed with respect to their relevance.

Montmorillonite intercalated with tetraethylammonium cation- DFT and IR study

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Organoclays are hybrid materials prepared by intercalation of organic cations, typically tetraalkylammonium cations, into interlayer space of clay minerals. The properties of organoclays can be controlled by a type and concentration of intercalated cation. Recently, the organoclays prepared from montmorillonite (M) and tetramethyl-, tetraethyl-, tetrapropyl- and tetrabutyl- ammonium cations (TMA^+, TEA^+, TPA^+, and TBA^+, respectively) were systematically studied using different experimental methods (Pálková et al., 2011). Further knowledge on distribution and orientation of organocations in the interlayer space of montmorillonite can be obtained by molecular modeling. In this work, structural and vibrational features of montmorillonite intercalated with TEA^+ cation were characterized theoretically and experimentally. Theoretical study was performed by means of the density functional theory (DFT) method. The obtained results were compared to data achieved by XRD analysis and infrared spectroscopy (mid-IR region). Calculated d_{001} interlayer distance (14.5 Å) agrees well with an experimental value of 14.2 Å. The analysis of the hydrogen bonds shows that the TEA cations are keyed into interlayer space of montmorillonite by moderate-to-weak C-H...O hydrogen bonds.

The calculated vibrational spectrum of the TEA-M structure is analysed in details. This study allowed unambiguous identification of the corresponding bands in the measured infrared spectra and their assignment to the particular vibrational modes. DFT molecular dynamic calculations revealed that the C-H stretching vibrational bands can change with respect to the d_{001}spacing of the TEA-M model indicating that CH_2/CH_3 stretching modes are very sensitive to environment.

The financial support for this research by the Slovak Research and Development Agency (Project APVV 0362-10) is gratefully acknowledged.

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Indexing theoretical Al-Si distribution in layer silicates – unit cell model for generality

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Unit cell based computational model was employed to simulate the Al distributions in tetrahedral site of layer silicate. The simulation was proceeding from convergence test with 3:1 Si-Al ratio to differentiate ratio of Si-Al 4:0 to 2:2 calculation. The method of simulation was averaging all counts of Al neighboring Si by counting all possibilities in each size and ratio. In simulation, Al-avoidance rule (Lowenstein's rule) and dispersion of charge were applied for restriction. Convergence (<2%) was achieved over 2x2 model and 2x2, 3x2, 3x3, 4x3 and 4x4 model of possibilities were simulated. From the comparing with existing ^{29}Si NMR data and HDC (homogeneous dispersion of charges) model, trend of data are similar but ~10% of error observed from simulation of this study in 4:0 to 2.5:1.5 Si-Al ratios. More Al content over 2.5:1.5 Si-Al ratio, there are no more perfect restriction of Al-avoidance rule.

Crystal structure refinement of Ge-incorporated akaganeite (β-FeOOH)

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Akaganeite is the naturally occurring form of β-FeOOH. It has since been recognized as a major Fe-oxide component in soils and geothermal brines (Holm et al., 1983) and as a corrosion product of some steels. A study of previous researchers (Buchwald and Clarke, 1989) suggests that akaganeite might act as a catalyst of corrosion. Both natural and synthetic akaganeite hardly occur single crystal showing spindle-shaped crystallites ranging 0.1 to 1.0 μm in size. Previous researchers (Song et al., 2010) found that Ge-incorporated akaganeite showed highly ordered and larger (~2.0 μm) size of crystallites. However, crystal structure of Ge-incorporated akaganeite is not clearly defined yet. In this study, we suggest crystal structure model of Ge-incorporated akaganeite by powder X-ray diffraction data and Rietveld method. Synchrotron powder X-ray diffraction data and the Rietveld method have been used to refine the crystal structure of Ge-incorporated akaganeite with the chemical ratio of Ge/Fe = 0.14 and Cl/Fe = 0.11 (Song et al., 2010). We try to propose a hypothetical akaganeite model refinement with Ge occupying the tunnel sites as $Ge(OH)_4$ based on crystallographic and chemical analyses, kinds of EXAFS regulation data. Finally the model chemistry imposed to $(Fe_{7.4}Ge_{0.6})O_{7.86}(OH)_{8.14}Cl_{0.74}(Ge(OH)_4)_{0.3}$. And refined cell parameter is monoclinic (*I* 2/m) with: a = 10.444, b = 3.018, c = 10.502, β = 90.33˚.

Freezing H_2O inside the tunnels of sepiolite – a cryo-NIR spectroscopic investigation

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Sepiolite has a periodically modulated structureof alternating 1 D tunnels and 2:1 trioctahedral ribbons [1]. Water exists as zeolitic (H_2O) or coordinated (OH_2) inside the tunnels and also associated to the SiOH groups on the external surface. The progressive dehydration of these species at elevated temperatures changes the structure and has a pronounced effect on the vibrational spectra [1-4].

This work extends the vibrational study of sepiolite from ambient down to -180 ^{o}C. For this purpose, a N_2-cooled cell accommodating ~15-20 mg of sample was coupled to a FT-NIR spectrometer via a diffuse-reflectance optical fiber bundle. Series of spectra were measured on samples with various initial water contents subjected to cooling and heating cycles. The temperature dependence of the position and width of several bands interrogating the tunnel water and the structural Mg_3OH are employed to observe freezing in confinement and its effect on the structure of the ribbons.

Financial support from the Applied Spectroscopy Laboratory of TPCI-NHRF and project POLYNANO-KRIPIS 447963/GSRT-Greece is gratefully acknowledged.

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Low temperature NIR spectroscopic characterization of palygorskite and indigo in synthetic maya blue

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Maya Blue (MB) is a famous historical Mesoamerican pigment with remarkable resistance to chemicals and weathering. MB was prepared by the Mayas from local palygorskite clay and leaves of an *Indigophera* plant. Modern studies suggest that the pigment can be synthesized by heating palygorskite and polycrystalline indigo (up to ~10 wt%) at temperatures (~400 K) causing the removal of zeolitic H_2O from the tunnels of palygorskite [1].

It has been suggested that the formation of MB proceeds by the quantitative self-assembly of the chromophore molecules in the tunnels of the clay ([2, 3] and refs. therein), but there is no consensus on the exact nature of the local structure and interactions involved.

This work compares synthetic MB and pristine palygorskite by variable-temperature NIR spectroscopy (100-300 K). In addition to reporting the manifestation of freezing on the spectra of palygorskite, this study explores the narrowing of vibrational bands at low-temperatures to study in unprecedented detail the indigo-palygorskite association chemistry. Based on these results, it is confirmed that the inserted chromophore is indeed indigo (and not any indigoid derivative) in very weak interaction with the tunnel walls of the clay host.

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Structural rearrangements of iron in Fe-PCH composites derived from Laponite – FTIR and Mössbauer spectroscopy comparative study

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Layered silicate composites were prepared through the surfactant directed assembly of organosilica in the galleries of synthetic layered hydrous magnesium silicate laponite, resembling closely the natural clay mineral - hectorite. Fe-containing porous clay heterostructures (PCH) were prepared by post-synthesis impregnation using two different Fe-sources, iron sulphate and iron citrate to obtain Si/Fe = 10.

In this work, the role of iron source on the textural parameters and acidity of the samples as well as the impact of such functionalization on the catalytic activity in the conversion of ethanol were investigated. Starting Na-Laponite (Na-Lap), iron exchanged (Fe-Lap) and thermally treated (Fe-Lap-550) were used as a reference to study sample evolution and structural rearrangements of iron in functionalized Fe-PCH composites derived from Laponite. The solids were characterized with the use of XRF, SEM, NH_3 TPD. The reliable information on the distribution of Fe ions within the PCH solid was obtained by comparison the FTIR analysis with the ^{119}Sn Mössbauer spectroscopy data. The structural changes of PCH were carried out in the MIR and NIR ranges and supported by the ^{119}Sn Mössbauer and ^{29}Si MAS NMR spectroscopies. Elemental analyses confirmed incorporation of iron into PCH structure. N_2 sorption revealed decrease of textural parameters, more pronounced upon impregnation with organic Fe source. FTIR indicates iron atoms incorporation into the network of amorphous silica developed during PCH synthesis. The tetrahedral sheets of Laponite were not affected by the transition metal cations.

The ^{57}Fe Mössbauer spectroscopy revealed two components of ionic Fe^{3+} in the Fe-Lap sample, both in tetrahedral coordination. Various QS values suggest slightly different surroundings of iron ions (much more defected or in the vicinity of the distorted environment). Calcination at 550 °C caused the appearance of an additional Fe^{3+} component and structural deterioration of the homogeneity of the sample compared to Fe-Lap. Impregnation of PCH structure by iron leaves some extra lattice Fe species as a distinct phase regardless of Fe source.

This work has received funding from the Polish-Norwegian RP operated by the National Centre for R&D under the Norwegian Financial Mechanism 2009-2014 PC No Pol-Nor/210445/53/2013.

General Session

Geochemical study of dolomite and smectite from non-marine bentonites (Bavaria, Germany)

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Bentonite deposits in Bavaria (Germany) associated with authigenic dolomite and calcite formed from Mg-poor rhyolitic volcanic ash in the Mid-Miocene Upper Freshwater Molasse. The chemical composition and strontium isotope ratios of carbonates and smectites from the Mittersberg (MB), Gabelsberg (GB) and Zweikirchen (ZW) deposits were examined using a 1 N HCl leach technique to trace the origin of magnesium, to resolve genetic relationships between carbonates and bentonite and to study the influence of the depositional environment. Palustrine dolomites (MB, GB) are characterized by high Sr (530 to 1120 ppm) and low Mn (300 to 580 ppm) contents, while pedogenic dolomites (ZW) have low Sr contents (210 to 370 ppm), but variable Mn contents ranging from 1700 ppm at the bottom of the bentonite to 370 ppm at the top. Groundwater calcites from the same deposit have lower Sr (66 to 126 ppm) and higher Mn content (2880 to 4720 ppm). The chemical composition of carbonates is influenced by variable redox conditions and evaporation processes in the palustrine-pedogenic setting.

The $^{87}Sr/^{86}Sr$ ratios of carbonates in bentonites are higher than in the precursor rhyolitic glasses (Horn et al., 1985). They show a regional trend with slightly lower values in the northern deposits (0.71042 to 0.71113, n=7; GB, MB) compared to the deposit in the south (0.71105 to 0.71154, n=6; ZW), suggesting distinct local Sr sources. Sr-poor groundwater calcites (ZW) have more radiogenic ^{87}Sr than Sr-rich pedogenic dolomites. This indicates significant changes in Sr isotope ratios of carbonate precipitating fluids within a deposit. The Sr contents of the exchangeable interlayer site in all smectites are very low (6 to 24 ppm). Their age-corrected Sr isotope ratios are slightly more radiogenic (0.71108 to 0.71285) than associated carbonates. Due to the low Sr contents, the Sr isotope composition of smectites is influenced more easily by post-formational isotope exchange reactions.

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Genetical signatures of nickel-chrome-bearing nontronite and montmorillonite in lateritised ultramafic rocks in the Muratdaği region (Uşak, Western Anatolia), Turkey

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Widespread lateritised ultramafic rocks in the Muratdağı region constitute a significant source of nickel for industry, but no detailed mineralogical and geochemical characterisations of these important materials have been performed to date. The purpose of this study was to fill this gap in the literature. The lateritic zones have developed in the uppermost levels of ophiolitic peridotites. The garnierite-bearing altered parts of the ultramafic rocks are enriched in smectite, Fe-(oxyhydr)oxide phases, and opal-CT. Micromorphologically, flaky smectite, and locally, Fe-rich particles, alunite, gypsum, gibbsite, and sulfur crystals developed along the fractures and dissolution voids. The development of saprolitisation suggests weathering, the presence of a silica cap, Fe-(oxyhydr)oxide phases associated with gypsum and alunite, and, locally, native sulfur occurrences along the fault systems are indicative of hydrothermal alteration processes. The ratio of Fe_2O_3+Cr_2O_5+Ni+Co/MgO increases significantly with increasing degrees of alteration. Thus, the alteration process(es) resulted in the formation of nontronite, Fe-rich and Fe-poor montmorillonite, serpentine, and locally Fe-rich kaolinite. Ni and Cr are concentrated significantly in altered units of laterites and are positively correlated with Fe_2O_3 content, controlled mainly by the formation of nontronite and Fe-rich smectite, and partially by serpentine and Fe-bearing kaolinite, as well as Fe-(oxyhydr)oxide phases. Consequently, Ni-Cr-bearing nontronite and montmorillonite precipitated authigenically from alkaline water rich in Al, Fe and Mg, under the control of both weathering and hydrothermal alteration process(es). The Fe, Al and Mg (associated Ni and Cr) required for smectite formation were supplied in solution(s) involved in the alteration of Ni-Cr-bearing olivine and pyroxene in the ultramafic host rocks.

This study was supported financially by the Scientific and Technological Research Council of Turkey (TUBITAK) in the framework of Project 110Y306.

Clay minerals in hemipelagic marl-limestone deposits – example of the latest Early Jurassic of the Lusitanian Basin (Portugal)

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The Toarcian (Lower Jurassic) it is well represented in the Lusitanian Basin (central-western Portugal) through marly-limestone succession accumulated in hemipelagic carbonate ramp setting (e.g. Duarte & Soares, 2002; Duarte, 2007). This work presents the clay minerals variations, in this sedimentary conditions, on a high-resolution context, in the eastern part of the basin between proximal (Tomar; ~ 70 m thick) and distal (Coimbra; ~ 280 m thick) sectors. The study involved the analysis of the Prado, S. Gião (further divided into its 5 members) and Póvoa da Lomba (only the base) formations in four reference sectors of the basin. The clay minerals composition of a total of 230 samples was investigated by the X-ray diffraction technique. The results show the domination of illite illite/smectite mixed-layer+kaolinite, among other discrete occurrences of chlorite and vermiculite. Besides the importance of the stratigraphic distribution of the different clay minerals assemblages across the Toarcian of the Lusitanian Basin, it is highlighted the decrease (locally, the disappearance) of kaolinite in the upper part of the series, revealing a clear change from humide to more aride conditions. By these results we emphasize the importance of clay minerals association in terms of the palaeoenvironmetal changes occurred after the Toarcian oceanic anoxic event (see Dera et al., 2009).

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Alteration of structural and physicochemical properties of clays under a 100 km overburden stress

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Structural alteration of clay minerals during compression (a decrease of “crystallinity” and dehydroxylation temperature) is a known phenomenon. Changes of crystal structure and particle morphology have been intensively studied (La Iglesia & Aznar, 1996; Plötze & Kahr, 2002). Some pressure-induced clay alteration effects remained, however, less understood, e.g. alteration of microporosity (<15 Å) or other physicochemical properties.

The goal of this study was to investigate the pressure influence on physicochemical properties of three clays: kaolin, sodium bentonite and illite. The measured parameters included the cation exchange capacity (CEC), the amount of leachable cations, the mean layer charge and the dehydration/dehydroxylation behaviour. Furthermore, changes in microstructural parameters like the specific surface area, the distribution of micropores (<15 Å) as well as “crystallinity” indices were studied. Experiments were carried out at 1.5 and 3 GPa during 24 and 96 hours.

Alterations could be observed in the microporosity of the clays and in the “crystallinity” of the clay minerals. The microporosity of kaolin was almost completely diminished after each compression state. The same was true for illite but after the longer compression. The microporosity of bentonite, however, showed a weak decrease only, i.e. the smectite interlayer as a part of bentonite micropores could be compacted only slightly, if at all. Nevertheless, the CEC of bentonite decreased up to 10% due to a lowered accessibility.

The pressure-induced alteration of compressed kaolinite, montmorillonite and illite was reflected in decreased “crystallinity” indices as well as crystallite size in *b*-direction (060). Further sign for alteration was an observed ditrigonalization of the octahedral sheet of clay minerals (Comodi & Zanazzi, 1995) causing a decreased dehydroxylation temperature (Vizcayno et al., 2005) and the intensity variations in infrared bands (Bell et al., 1991).

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Characterisation of clayey raw materials for Bronze Age ceramic manufacture in Turopolje (Croatia)

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A Bronze Age ceramics and possible raw materials in the area of Turopolje in northwest Croatia have been studied. The main goal of this study is to determine the availability and types of raw materials, as well as to reconstruct the technological processes (preparation of raw material and firing technique) of pottery making at archaeological site Kurilovec-Belinščica (Virovitica cultural group dating from 15-12 century BC, i.e. the end of the Middle Bronze Age and the beginning of the Late Bronze Age). For this reason three clayey materials, outcropping in the vicinity of the archaeological site, were collected. Two sampling locations were found close to the settlement (both at a distance of about 600 m) and one is the clay pit, located about 4 km from the archaeological site, which is currently in exploitation for brick production. Detailed mineralogical analyses were performed for four samples of clay materials (XRD, STA; grain size analysis), 16 samples of experimental ceramics made from these materials (XRD, OM), as well as 26 samples of ancient ceramic shards (XRD, OM, STA, IR). Comparison between the data obtained from the analyses of potential raw materials and those obtained from the analyses of the experimental and archaeological ceramics will be reported. Possible archaeological implications, such as the extent of environmental influence on technological processes (availability of raw materials) and socio-economic factors (matter of choice), will be discussed as well.

Smectite in ancient pottery from Hallstatt – a contradiction?

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250 million years ago the area around Hallstatt was covered by a large ocean. Even at that time climate change was a fact: Due to global warming water evaporated and huge amounts of salt crystallized. 7000 years ago people discovered these salt deposits, settled in Hallstatt and started salt mining. Pottery was used in everyday life and also as grave goods. During the last 200 years archeologists excavated various ceramic products and many potsherds from Bronze Age, Iron Age and Roman times.

For this study about 30 different shards and samples from some clay pits in the surrounding of Hallstatt were selected and analyzed. Bulk and clay mineral composition of shards and potential raw materials were determined by X-Ray Diffraction (XRD) and Simultaneous Thermal Analysis (STA). Cation exchange capacity of all samples and grain size distribution and consistency limits of the raw materials were measured. Trace elements were analyzed by ICP-MS to obtain information about the provenance of the raw material for the pottery.

Against expectation the trace element composition of the clay samples and the pottery did not match. This proves that the pottery was not produced in Hallstatt, but imported in exchange for the salt.

The mineral content of pottery depends on raw material, possible additives and firing temperature. Clay minerals from the raw materials are transformed into new silicate minerals during the firing process. Especially smectites and vermiculites are very sensitive to temperatures above 550 °C. At this temperature an irreversible dehydroxilation occurs.

Surprisingly considerable amounts of smectite were detected in some of the analyzed shards. It seems implausible that the firing temperature did not exceed 550 °C, because such pottery would not be durable and it is well known that the kilns allowed much higher temperatures.

The most probable explanation is that during thousands of years of burial in the soil of Hallstatt smectite did recrystallize. The further investigation of pottery from different areas and different times produced under different conditions should help to understand this clay mineralogical contradiction.

Mineralogic-chemical and physical characteristics of the peloids in Muğla region (South-western Turkey) – suitability for use in pelotherapy

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The study conducted on peloids used spas in Muğla city region (south-western Turkey) included the investigation of mineralogical, physico-chemical and geochemical properties of two types of peloid samples in order to assess the suitability of the material for healing and aesthetic-related purposes. In situ formed muds have been used in therapy and thermal baths since prehistoric times for the treatment of some diseases, and also for relaxing and beauty purposes. The mineralogical characteristics of the thermal muds are compatible with the origin of the material. Both of the sediments are fine- to medium sized, and composed mostly of carbonates, clay minerals, quartz, and partially feldspar, serpentine, gypsum, halite, and rarely pyrite. The mineralogical composition of the muds controls their physico-chemical properties. Anion, e.g., Cl, Br, and SO_4 contents in the thermal waters is extremely high in the mud of the first group, which from near the sea. Major and some trace element concentration in the samples are similar. Co, Cr and Ni concentrations are higher than in pharmaceutical clays and average clay. The high element concentrations reflect the chemical composition of ultrabasic rocks around the spa center. The concentrations of Cu, Mn, Ti, Zn and partially Pb are slightly higher than those of the pharmaceutical clay, but within acceptable limits. The concentrations of some hazardous elements, e.g, As, Cd and Hg are higher than in the above mentioned pharmaceutical clay, especially in one of peloid, and also in the thermal water. The anion contents of the water are related to sea water interaction. The element concentration is influenced by an active fault system, present in the area. The moderate content of clay minerals and high content of non-clay minerals reduces BET surface areas, cation exchange capacity, plasticity, adsorption, viscosity, and cooling kinetics. The characteristic parameters of the mud are comparable to some commercial muds, already successfully used for medicinal purposes. However, some dangerous element contents may lead to health problems and the non-clay mineral content can cause discomfort for the skin.

Characterisation and distribution of carcinogenic amphibole and serpentine minerals and relationship with development of potential mesothelioma cases in Eskişehir, Western Turkey

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Amphibole group minerals occur in Paleozoic metamorphic units and serpentine minerals occur in Triassic ophiolitic units in the Eskişehir area. Silicification, iron (oxyhydr)oxidation and chloritisation are generally associated with serpentinisation. Characteristics of metamorphic and ophiolitic units in the region and related amphibole and serpentine occurrences using polarised-light microscopy, X-ray diffraction, scanning and transmission electron microscopy, differential thermal analyses - thermal gravimetry, infrared spectroscopy, Raman Spectroscopy, geochemistry (chemistry, and stable isotope) methods suggest the development of fiber/asicular, tremolite and actinolite type amphibole and chrysotile type serpentine with the average structural formulae of
$(Si_{7.62}Fe_{0.3}Al_{0.08})(Mg_{5.01}Fe_{0.07}Ti_{0.01}Mn_{0.004})(Ca_{2.03}Na_{0.05}K_{0.03})O_{22}(OH)_2$,
$(Si_{7.81}Al_{0.19})(Mg_{2.25}Al_{1.21}Fe_{1.09}Ti_{0.1}Mn_{0.008})(Na_{1.04}Ca_{0.43}K_{0.24})O_{22}(OH)_2$, and
$(Si_{3.79}Al_{0.13})(Mg_{5.55}Fe_{0.41}Mn_{0.002})O_{10}(OH)_8$, respectively.
Based on H and O isotope data, tremolite and chrysotile developed from tectonic controlled magmatic and meteoric hydrothermal systems. Eskişehir villagers were exposed to asbestos either occupationally or environmentally. Mesothelioma cases in the Eskişehir region exhibit positive correlation with the crystal dimention and concentration of tremolite as compared to that of chrysotile. However, the non-existence of genetic data and the possible role of genetic factors together with the environmental effect on the development of mesothelioma are unclear.

This study was supported financially by the Scientific and Technological Research Council of Turkey (TUBITAK) in the framework of Project 112Y245.

Influence of synthesis method in preparation of organosmectites

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Organically modified clays (‘organo-clays’) have attracted a great deal of interest because of their wide applications in industry and environmental protection. Intercalation of cationic surfactants hexadecylpyridinium ($HDPy^+$) and hexadecyltrimethylammonium ($HDTMA^+$) into the interlayer space of homoionic (Na-, Ca- and Zn-) smectites using tree methods (conventional method, solid-solid reactions and microwaves irradiation) was investigated in this study. The changes in the surfaces and structures of the modified-smectites with HDTMA surfactant were characterized using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

The results showed that the intercalation of surfactant cations was complete within 120, 15 and 2 minutes by conventional method, solid-solid reactions and microwaves irradiation, respectively. $HDPy^+$ and $HDTMA^+$ surfactants were retained by Zn-exchanged smectite suggesting important surface properties (CEC=80 meq/100 g clay, S_{BET}=116.5 m^2/g) and acid-base properties (point of zero proton charge PZC, density charge σ_H). HDPy cation loading was effective suggesting that the aromatic polar group is favored for intercalation. Different configurations of surfactants within smectite interlayer were proposed based on the basal spacings which increased with surfactant loading. The presence of symmetrical and asymmetrical vibration bands of the -CH2 group in the IR spectrum of the modified clays and the variation of their frequencies and their intensities confirmed the results obtained by XRD.

Mineralogical investigation of tailing materials from historic Saxonian mining sites by X-ray powder diffraction

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Historic Saxonian mining tailings (located in Freiberg and Altenberg) exhibit a complex mineralogical composition and bear potential contents of valuable metals and minerals. For any further economic considerations, the detailed knowledge about the mineral distribution with respect to the grain size is essential. However, due to the large variety of minerals (i.e. several types of sheet silicates), the quantification of the phase abundances is a challenge.

Both sites contain fine-grained, water saturated muddy material. For the analyses certain segments of the drilling cores were chosen for the analyses. The samples were sieved into appropriate size fractions (100 µm, 63 µm and 20 µm). The <2 µm fraction was separated by the use of the Atterberg method. Powder XRD specimens were prepared by grinding about 3 mL material in a McCrone micronizing mill for 10 min with 10 mL ethanol. Measurements were run with Co-radiation, Fe filter, automatic divergence slit and semiconductor strip detector. Oriented specimens of the <2 µm fractions, prepared by sedimentation onto glass slides, were measured with Cu-radiation, automatic divergence slit and secondary beam monochromator with scintillation counter.

Tailings of the Altenberg tin Greisen deposit are dominated by quartz, topaz, micas, and a small content of other layer silicates. Cassiterite is still detectable and quantifiable (≈ 0.7 wt% in the <20 µm fraction). Hematite and cassiterite are enriched in finer fractions. The <2 µm fraction reveals kaolinite and a small amount of dickite and chlorite. The material from the Freiberg hydrothermal Pb-Zn-Ag deposit mainly contains quartz, micas (≈ 30-40 wt%), chlorite, sulphides, and carbonates. The sulphides (pyrite and marcasite) are concentrated in the <20 µm fraction (≈ 24 wt%). Remarkable is a high content of chlorite with (up to 10 wt%). The oriented specimens allow identification of micas, chlorite and kaolinite.

Brick kilns and clay pits of northeastern Lower Austria – History and mineralogical characteristics

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More than 500 brick kilns and clay pits are recorded as operating since the beginning of the 18th century in the districts of Mistelbach and Gänserndorf (RAMML, 2014).

A large variety of historical sources, along with the unique seal that each kiln impressed on the bricks it produced, enable us to trace the history of most of the kilns and their ownership. The brick industry has undergone dramatic changes since the end of World War II. Originally based largely on handcrafting, the production process was gradually transformed and is now almost fully automated and concentrated in big production sites. As the result of this process the last operating kiln in this district was shut down in 2009.

The studied area, covering approximately 2500 km^2 in total, belongs to the Molassezone in the west and to the Vienna Basin in the east. Both geological units are covered by loess in abundance.

From a historical point of view loess and loamy loess deposits provide by far the main source of raw material for all kind of bricks.

The sediments of Neogene age became more and more important as brick clays with the development of the ring kilns from the late 19th century onward.

In the Molassezone the most widely used material was the Karpatian marine Laa-Formation (PILLER et al., 2004). In the Vienna Basin the Lower Badenien marine Lanzhot Formation and the Pannonian limnic-fluvial Gbely-Formation (PILLER et al., 2004) were most important.

Bulk rock composition, clay mineralogy and grain size analyses were carried out in order to describe the diversity of the brick clays.

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Reactivated timings of some major faults in the Chugaryeong fault zone since the cretaceous period

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Recently developed illite-age-analysis (IAA) approach has been applied to determine the multiple events for the Singal and Wangsukcheon faults in the Chugaryeong fault belt, Korea. Fault reactivated events during Late Cretaceous to Paleogene events (69.2±0.3 Ma and 27.2±0.5 Ma) for the Singal fault and of 75.4±0.8 Ma for the Wangsukcheon fault were determined by combined approach of the optimized illite-polytype quantification and the K-Ar age-dating of clay fractions separated from the fault clays. These absolute geochronological determinations of the multiple tectonic events recorded in the Chugaryeong fault belt are crucial to establish the tectonic evolution of the Korean Peninsula since Late Cretaceous.

Thermodynamic stability of trioctahedral chlorites of Mg-Fe isomorphic series (by thermochemical data)

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Chlorites $(Mg,Al,Fe)_6(Si,Al)_4O_{10}](OH)_8$ are widespread layered rock-forming minerals found in magmatic, metamorphic, hydrothermal and sedimentary rocks. The samples of chlorites from three Russian deposits were studied. On the basis of X-ray electron microprobe analysis their chemical formulas were calculated on the basis of 22 charges: $Mg_{4.9}Fe^{2+}{}_{0.3}Al_{0.8})[Si_{3.2}Al_{0.8}O_{10}](OH)_8$ (I) (Krasnoyarsk Krai, East Siberia), $Mg_{4.2}Fe^{2+}{}_{0.6}Al_{1.2})[Si_{2.8}Al_{1.2}O_{10}](OH)_8$ (II) (Tuva, East Siberia) and $(Mg_{4.0}Fe^{2+}{}_{0.8}Al_{1.2})[Si_{2.8}Al_{1.2}O_{10}](OH)_8$ (III) (Zlatoust, Middle Ural). According to modern Nomenclature of chlorites (Guggenheim et al., 2006) the studied samples were classified as intermediate members of the Mg-Fe isomorphic series of clinochlores. Results of X-ray diffraction and FTIR-spectroscopy confirmed the monomineralic composition of the samples. Thermal analysis in the range from 20 to 1000 ^{o}C showed the characteristic behavior of clinochlore. The total mass loss (removal of constitutional water) was about 13%. The thermochemical investigations were carried out using a Calvet microcalorimeter “Setaram”. The enthalpies of formation from the elements were determined by the high-temperature melt solution calorimetry method. The values of $\Delta_f H^o$(298.15 K) were obtained as -8811 ± 11 (I), -8748±24 (II), and -8674±13 (III) kJ/mol. The standard entropies S^o(298.15 K) of the studied clinochlores were estimated using reference data on the entropy of clinochlore $Mg_6Si_4O_{10}(OH)_8$ (Robie and Hemingway, 1995). The values of $\Delta_f G^o$(298.1 K) calculated on the basis of these entropy values were found to be -8153 (I), -8091 (II) and -8020 (III) kJ/mol. The obtained data show that the Gibbs energy of formation of clinochlores increases with increasing iron content in their composition, corresponding to a decrease of the thermodynamic stability of clinochlore with increasing iron content.

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Surface controls for the anti-inflammatory activity by naturally-occurring halloysite

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Halloysite is a clay mineral of the kaolin group that traps cationic agents in the hollow lumen of the tubes in spite of sharing low cation exchange capacity and specific surface area values. These properties of halloysite has been recognized and considered as an attractive material in the areas of biotechnology, pharmaceutical, and medical research, and for developing technologies related to cancer cell separation, bone implants, cosmetics, control drug delivery, dentistry and bone tissue scaffolds, vehicle drug delivery systems, enzymatic nanoscale reactors, stem cell attachment and proliferation devices, adhesion of human dermal fibroblasts, with fibroblasts maintaining their cellular phenotype and spreading. The present paper compares the anti-inflammatory and cytotoxic activity of halloysites from eight different locations, including four studied elsewhere, namely halloysite collected from Barton Locality, South Australia; Perth, Kalgoorlie, Western Australia; Bay of Plenty, Northland, Waikato, New Zealand. The 12-O-tetradecanoylphorbol-13-acetate (TPA) method was conducted. Also, the mieloperoxidase (MPO) enzymatic activity, a specific marker for migration and cellular infiltration, was quantified. Cell viability and cytotoxicity was determined by the reduction of tetrazolium as induction step and the MTT bromide assay. Unlike kaolinite, concluded to be lethal to rats on prolonged exposure in high concentrations, halloysite has shown potential health benefits, with edema reaching maximum levels only after 4 h. The anti-inflammatory activity of halloysite at t = 4 or 24 h surpassed that for indomethacin. The extent to which halloysite inhibited the number of neutrophiles that infiltrated the inflammation site was as high as 82.4% (4 h) and 86.83% (24 h) more relative to samples containing TPA only. Several halloysites showed higher edema inhibition values at longer reaction times, enabling active surface sites leading to a higher effectiveness of migration and cellular infiltration. A direct relationship between the anti-inflammatory activity and cytotoxicity and surface area (but not surface charge) of halloysite became apparent.

Geological, mineralogical and geochemical characterization of the Miocene zeolite-bearing volcaniclastic sediments, Ankara, Turkey

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The study area is located in the Tuzgölü basin in central Anatolia. Early Miocene andesitic-dacitic tuffs were deposited within lacustrine and fluvial environment in the region. Zr/TiO_2-Nb/Y plot indicates that the vitric tuffs are of dacitic and andesitic composition. The lacustrine sediments are composed of unaltered vitric tuffs as well as of tuffs altered to the following diagenetic facies: (1) bentonite, (2) interbedded bentonite (3) clinoptilolite/heulandite, (4) chabazite, and (5) analcime. The clinoptilolite is the most widely distributed authigenic phase in the unwelded tuff beds, typically containing clinoptilolite and heulandite, erionite, smectite, plagioclase, K-feldspar and opal-CT. Chabazite beds are composed of nearly pure chabazite in the unwelded tuff beds overlying the clinoptilolite beds. K-feldspar (sanidine), oligoclase, anorthoclase, andesine and rarely albite minerals were identified in the tuffs. Based on the petrographic and microprobe analysis feldspars in the unaltered tuffs show generally an oligoclase-andesine composition, and authigenic K-feldspar is mainly observed together with clinoptilolite and partly clinoptilolite+erionite. Mineral associations and close chemical relationship between tuffs and bentonite beds indicate that the alteration of the pyroclastic material appears to have proceeded in a temporarily closed basin. RE, LIL, HFS, and partially TR elemental compositions of the zeolitic tuffs are generally similar to the chemistry of stratigraphically equivalent vitric tuffs and the source volcanics, suggesting that zeolite diagenesis took place in a mostly closed hydrologic system. At some levels, two or three zeolite minerals, e.g., clinoptilolite/heulandite, erionite, and chabazite were observed as coexisting minerals or form nearly pure zeolite-bearing layers. The $d^{18}O$ and dD content of the clinoptilolite minerals and smectites are between 14.0 and 20.7‰, and 73.0 and -85.7‰, range from 17.4 to 19.3 and from -84.2 to 96.6‰, and respectively. Accordingly, the temperature of formation of the clinoptilolites was calculated to a range between 34.2 ºC and 67.0 ºC, and that of the smectites for 45 to 54 ºC. So the isotopic compositions of the minerals suggest that the minerals were formed at low to moderately low temperatures in similar environmental conditions.

Industrial clays

Identification of sodium carbonate activated bentonites

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A large amount of bentonites is used because of its rheological properties such as thixotropy. Examples are drilling mud and paint additive. The rheological properties strongly depend on the type of interlayer cation balancing the permanent charge of the smectites.

While few bentonites (smectites) are dominated by exchangeable Na^+ the rheological properties of Ca/Mg-rich bentonites are improved by adding sodium carbonates for the exchange of natural interlayer cations by Na^+. For this activation (sometimes referred to as alkaline or in German also referred to as soda activation) different amounts of different sodium carbonates are added. The dosage with respect to Na^+ ranges from a few % of the CEC to slightly above the CEC corresponding to 1-5 mass% Na_2CO_3. Also the water content may vary from the dried state at which the actual activation (cation exchange) does not take place up to the presence of excess water leading to a complete reaction.

Natural Na-rich bentonites and alkaline activated bentonites are rather similar in many properties. So far suitable methods to unambiguously distinguish natural Na-rich bentonites from alkaline activated materials were missing. Therefore, based on the study of Steudel et al. 2013, in the present study different methods were tested to distinguish both. This is relevant not only for customs but also for research and development. The most important conclusion of the present study (Kaufhold et al. 2013) is that the presence of any peak or intensity around 200 °C in the MS-CO_2 curve indicates technical activation of bentonite with sodium carbonate. Findings were supported by CEC measurements.

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Characterization of the bulk and microrheological properties of arrested states in dilute natural clay mineral dispersions

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Dispersions of clay minerals display a rich variety of rheological behavior mainly because of the complex arrangement of anisotropic disk-like colloidal particles due to the electrical double layer surrounding them. Depending on solid content, pH and electrolyte concentrations clay mineral dispersions form either fluid, gel-like or glassy structures. The aim of this study is characterization of the difference of the arrested states of natural and synthetic smectite dispersions using bulk and microrheology. The purified and well characterized natural hectorite and montmorillonite (0.2 µm fraction of SHCa-1 Source Clay and Volclay) were used to enable characterization of their rheological properties accurately.

While the phase transition of Laponite (synthetic hectorite) dispersions is well understood [1], it is not known exactly for the natural clay mineral dispersions. Using rotational and oscillatory shear rheometry we have observed that the sol-gel transition of Laponite suspension at high ion concentration (10^{-2} M) occurs only with 1 wt% solid concentration, while for the natural smectite samples the sol-gel transition was shifted to higher solid concentrations, 3 wt% of hectorite and 7 wt% of montmorillonite. The storage G' and loss G'' moduli of the two types of clay suspensions have been determined in a broad frequency range (10^{-2}-10^{4} rad/s). The clay mineral content was varied between 1 and 7 wt% depending on material and salt concentration was varied between

10^{-4} and 10^{-1} M. The moduli increase with increasing solid and electrolyte concentration. But the effect of solid concentration is more pronounced than the effect of ionic strength. For the both arrested gel and glassy states G' is always much larger than G''. For this reason differences in structural heterogeneity of arrested states was investigated on micro length scale using the optical multiple particle tracking technique, MPT. It was observed that building of the repulsive glassy structure takes a longer time (~150 h) than the formation of attractive gels (~5 h). Using fluorescent tracer particles of different size (0.21, 0.52 and 1.01 µm) the MPT method enables us to elucidate the micro-structure of arrested states.

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Improved quality control of basaltic crushed stone

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Basaltic materials (such as basalt, basanite, or diabase) are often used to produce crushed stones which in turn are used in asphalts for road construction or as track beds. These rocks, however, may contain glass which at least partly converted to swelling clay minerals (smectites) which in turn may affect the quality of the crushed stones. The prerequisite for using crushed stones for road or track construction is the stability or the integrity, respectively, even in the wet state. Smectites contacted with water exert a certain swelling pressure which may result in disintegration. Therefore, the smectite content is determined in the run of standard quality control (e.g. by measuring the CEC). However, the CEC (or the smectite content calculated from CEC) does not always explain the different stabilities of different samples. This could be related to a different accessibility of the smectite surfaces with respect to water and/or the CEC solution. For CEC measurements the sample is commonly ground. The stability of the sample, on the other hand, concerns the uncrushed state. Based on comparing stability tests with CEC measurements of different grain size fractions the special role of isolated smectites was identified. Those samples with satisfying stability despite the presence of some smectites commonly contained hydraulic inactive smectites which means that neither the water nor the CEC solution could reach the smectite. These samples had to be ground to measure the maximum CEC and the difference between the CEC of 1-2 mm particles to the CEC of powders was much larger compared to other materials with less hydraulic inactive smectites. The present study, therefore, showed that the determination of the CEC of both granular samples and powders may help to distinguish hydraulic active and inactive smectites in the basaltic materials (Kaufhold et al., 2012).

Kaufhold, S., Dill, H.G., Dohrmann, R. (2012) Clay mineralogy and rock strength of a mid-German diabase - implications for improved quality control. - Clay minerals, 47, 419-428.

Effect of two organophilic modifiers on properties of organoclay-polymer nanocomposites

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Organically modified layered silicates have been widely studied for the past decade as property enhancers for polymeric materials. Progress in mechanical, thermal, flame resistant, barrier and other properties of thermoplastics has been achieved by addition of organically modified layered silicates to polymer matrices to prepare Polymer-Layered Silicate Nanocomposites (PLSN). The filler content can be as low as 2-6 wt.%. Due to property enhancement even at small clay loadings, the PLSN systems possess several advantages compared to conventionally filled polymers, such as lower weight; enhanced flame retardant and thermal stability, superior barrier properties without requiring a multi-layered design, etc. Trioctylammonium (3C8) and tetraoctylammonium (4C8) were selected to prepare the organo-clays from a sodium-saturated <2 μm fraction of Jelšový Potok (JP) bentonite (Slovakia). The d_{001} values depended on the size and structure of the organo-cation. The height of the interlayer space was 1.1 and 1.3 nm in 3C8JP and 4C8JP, respectively. Infrared spectroscopy in the mid-IR (MIR) and near-IR (NIR) regions was further used for organo-clay characterization. The positions of the CH_2 stretching bands were similar, the intensities slightly increased for 4C8 due to higher number of alkyl chains. Based on the fundamental vibrations observed in the MIR region, the first overtone ($2v$XH) and combination ($(v+\delta)$XH) modes of XH groups (X = O, C, N) were identified. The changes in the intensity of the $(v+\delta)H_2O$ band near 5250 cm^{-1} allowed for comparison of the amounts of water adsorbed on the organo-clay surface. The NIR showed the $2vCH_3$ and $2vCH_2$ bands in the 5900-5500 cm^{-1} region. The combination $(v+\delta)NH^+$ mode near 4750 cm^{-1} allowed identification of NH^+ groups in 3C8 which were difficult to recognize in the MIR spectrum due to overlapping with other bands. Rheological measurements were used for assessment of these materials for application as fillers in nanocomposites with polyethylene, polycaprolactone, or polyamide matrix. Ultimate properties strain at break and tensile strength differ significantly depending on the filler modification. The positive effect was higher for clay modified with larger cations, the most efficient modifier was 4C8.

Supported by the Slovak Research and Development Agency, grant APVV-0362-10

Metronidazole/montmorillonite nanodevices for controlled drug delivery

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In the present work the potential of a new-tailored made drug delivery system, obtained by the intercalation of the antibiotic metronidazole (MNE) into the K10-montmorillonite clay (MMT) has been evaluated.

The interest in this field comes from the consideration that the pharmacokinetic profile of the conventional tablet metronidazole indicates that the dosage form not only provides minimal amount of metronidazole for local action but it also holds unwanted systemic effects. This way, the design of more effective strategies for the administration of metronidazole, aiming at minimizing secondary effects, increasing drug bioavailability and stability or even exhibiting high accuracy in reaching the target has become significant.

In this perspective a series of MNE/MMT hybrids have been prepared by varying the pH and the amount of loaded drug. Complementary kinetic and equilibrium studies have been carried out in order to elucidate the adsorption mechanism of the MNE into the MMT and to establish the nature of the interactions involved in the hybrid MNE/MMT formation. Moreover, the interactions sites of the clay surface have been proposed on the bases of the XRD results.

The gathered results allowed us to establish that the adsorption process strongly depends on the pH conditions and to propose a multistep adsorption mechanism involving the neutral and the cationic form of the drug, which interact with different sites of the clay surfaces, i.e. the interlayer region and the faces of the lamella.

The drug release kinetics has been then studied under physiological pH mimicking conditions simulating the oral drug administration and delivery. The investigation of the release profiles and the comparison with the commercial formulation of the drug reveal not only that the new-tailor made formulation could be fruitful exploited for successfully prolonged the action of drug in the target site but the use of these nanodevices reduce both time and costs for the drug delivery.

Characterization of ceramic clays from Corumbataí formation used in the ceramic district of Santa Gertrudes (CDSG) – Brazil

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The production of ceramic tiles in Brazil reached almost 1 billion m² in 2013. More than 60% of the tiles was produced in the CDSG. The main advantage of the ceramic industry from Santa Gertrudes district is an application of the dry grinding process, which is much more profitable than the wet grinding which is used worldwide. The dry grinding process accounted for 73% of the tiles production in the CDSG in 2013. For the dry route of tiles production only rocks from Corumbataí Fm. in the region are used, which decreases costs for raw material transportation. On the other hand, the booming ceramic industry in the Santa Gertrudes district has caused air pollution and river silting due to the large amount of dust generated by drying and transportation the raw material. Ceramic companies need to replace their current beneficiation areas by industrial dryers. However, the batch whose raw materials were drying forced has produced tiles that break or crack during the industrial process. Three types of raw materials D (slightly weathered), I (weathered) and M (highly weathered) were examined in the present study in order to better understand the behavior of clays during drying process. The quantitative XRD analysis showed that D, I and M contain 49, 60 and 59 wt.% of clay minerals, respectively. Illite and smectite are the main minerals, probably with a small amount of mixed-layered illite-smectite. Sample M contains also kaolinite that according to XRD analysis may be accompanied with mixed-layered kaolinite-smectite. Thermal experiment was realized in different temperatures (100 °C, 200 °C and 300 °C) for fraction <2 µm. Air dried XRD pattern indicated the collapse of smectite over 100 °C. After 200 °C and 300 °C the ethylene glycol pattern presented the same behavior as for samples with no thermal treatment. Technological tests realized with tiles made by D, I and M raw materials dried by sun, and at 100 °C, 200 °C and 300 °C showed that linear drying shrinkage decrease as the temperature increase. Bending strength also decrease and some tile shows cracks at 300 °C. Therefore, the raw material that was dried over to 100 °C changed the ceramic behavior. It is probably due to plasticity loss caused by dehydration of smectite. Although, ethylene glycol treatment keep the XRD pattern behavior, showing that smectite collapses could be reversible up to 300 °C.

K, Ca-Na feldspar, firing schedule and mixing type effects on cristobalite formation in kaolinitic and illitic clays of Westerwald

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Three Westerwald clays HB(kaolinitic), KW(illitic) and P1(naturally mixed illite and kaolinite) (Kromer, H., 1980) were selected for this study. All individual clays and wet and dry mixtures of HB-KW (HB3+KW1, HB2+KW2, KW3+HB1) were heated with different rate and soaking time at succesive temperatures up to 1250 °C. X-ray determinations were made on all samples heated with dynamic and static heating experiment. The intense cristobalite lines are observed in pure HB after 1150 °C. Above 1150 °C, the amount of cristobalite decreased as KW content increased in the mixtures. Cristobalite was never observed in pure KW rich and KW rich mixture. Cristobalite also was never observed in P1 and wet mixed HB2-KW2 mixture in static heating, contrasting strongly with its prominent development among the high temperature phases of dynamic heating of P1 and HB2+KW2. A small amount of quartz is presumed to be converted into cristobalite. The main amount of cristobalite formed from the expulsion of excess SiO2 from HB. Increasing amounts of cristobalite are determined by peak temperature, prolonged soaking time, lower heating. On the other hand the effect of these parameters depends on type of mixing and mixing ratio of HB-KW. The effects of these parameters are more pronounced in HB3+KW1. Comparative studies were carried out to evaluate the influence of 20% K or Ca-Na feldspar addition on the cristobalite formation. Cristobalite peaks intensities were shown to be decreased with dry and wet mixing of Ca-Na feldspar-and K feldspar with pure HB, while totally disappearing cristobalite peaks could be observed in wet mixed HB3+KW1- 20% K or Na-Ca feldspar sample. Cristobalite formations in pure HB and mixed samples (P1 and HB2+KW2) are observed at 1200 °C and 1100 °C respectively in dynamic heating and increased with cooling. In contras to cristobalite appearance at higher temperature 1200 °C in pure HB described above, mullite appearance temperature 1100 °C is 50 °C lower than those observed in pure HB in static heating experiment.

Kromer, H., 1980. Geol. Jb. D. Rhei D Hanover, 69– 84 (Ton HB no 105 Ber. dt. keram. Ges., 55, 7) (Ton KW no 56 Ber. dt. keram. Ges. Geol.) (Ton P 161 no 75 Ber. dt. keram. Ges)

Bentonite – a natural additive in lime-metakaolin mortars for restoration of historic buildings

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There is an evident presence of a significant heritage of adobe construction in Portugal, with a special territorial focus on the area between Murtosa and Figueira da Foz. Currently many edifices constructed from adobe bricks still persist, both in city centres and in rural areas. Unfortunately, the degradation has affected many of these buildings and this is particularly evident in terms of the renders, because they are the exposed external element and extremely prone to the action of weather.

The work evaluates the behaviour of mortars based on lime, looking for their application as renders for restoration of adobe walls. Mortars with binder: aggregate 1:3 volumetric ratio were prepared as is traditionally used in old buildings in central parts of Portugal. Due to the specificity of the support, natural clay bentonite (5 wt.%) and artificial clay metakaolin (20 wt.%) were used as additives to air lime mortar. Three types of blended mortars (BAL, AL20MK, BAL20MK) were prepared besides the air lime (AL) reference mortar. Mortar prisms 4×4×16 cm were analysed in a view of mechanical properties and salt resistance. Furthermore, the mortars were placed in three traditional ways on old adobes taken from demolished houses and their behaviour was tested by artificial accelerated ageing. Finally, mortars were applied on a wall made from adobes, where panels 40×40 cm were monitored and trials with adhesion strength and Karsten tubes have been conducted. The results achieved by comparison of the characteristics from all the experimental procedures indicate that mortar comprising air lime and 5 wt.% of bentonite accomplishes in the best way the requirements in its use as render of adobe structures.

Mineralogical study of different kaolin samples from Iran China Clay Company and possibility of ultrasound irradiation as useful treatment in future procedures

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In this research, kaolin samples which are used in the ceramics industry were examined mineralogically and the possibility of using ultrasound irradiation as a useful pretreatment in processing investigated. Three types of kaolin samples were provided (by the Iran China Clay Company) which can be classified based on the quality of the kaolin with respect to chemical analysis of major oxides such as Al_2O_3, SiO_2, CaO and Fe_2O_3. These kaolin samples were classified into three types: normal kaolin (A), kaolin enriched with calcite (B) and kaolin (C) in which considerable amounts of calcite and iron impurities were found. The CaO contents in kaolins A, B and C were ~1.5%, ~4.35% and ~3.5%, respectively; the Fe_2O_3 content in kaolins A and B was ~0.5% but was up to 1% for kaolin C. Kaolin A is currently used as a raw material in a processing plant; to investigate crushed-ore samples, ~300 kg of samples were taken systematically from milled powder (before feeding to the washing plant) and also from the final product out of the processing plant. The amounts of Al_2O_3 in the milled powder and final product are ~23% and ~15%; note that ~63% and 74%, respectively, of SiO_2 was also found in these samples.

Detailed mineralogical studies including investigation of thin and polished sections not only for each size fraction (up to 38 mm) but also for crushed samples were carried out. X-ray diffraction analysis was used and compared with chemical analyses and mineralogical assessments to estimate the amounts of major minerals present.

After preliminary investigation of various approaches for improvement in the quality of the final product from the processing plant, the possibility of using ultrasound irradiation as a useful treatment in washing procedures and elimination of impurities (such as calcite, silica and iron-containing minerals) was examined.

Formation of hydrotalcite coating on the aluminum alloy in spray system

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Hydrotalcites, or layered double hydroxides are fundamentally anionic clays. In a broad range of compositions are possible of the type denoted as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+} A^{n-}_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are di- and trivalent metal ions, and A^{n-} is the interlayer anion, x is the trivalent cation substitution degree, and takes values in the range 0.2 £ x £ 0.33.

In relation with coating application, HTs have been widely studied in corrosion research as anticorrosive inhibitors loaded with different anions (Lin and Uan, 2009; Williams and McMurray, 2003; Buchheit et al., 2002, Buchheit and Guan, 2004). However, most of the experiments were taken by dipping in solutions or in autoclave, which limit their industrial applications. Here we report a spontaneous and speedy formation of Li-Al hydrotalcite on Al alloys in spray system.

The coatings were formed on Al panels by exposing them in alkaline lithium salt solutions containing either carbonate, nitrate, or nitrate/persulfate additions in a spray system. A well-crystallized hydrotalcite-like phase was characterized by SEM in the coating layer. Li-Al hydrotalcite crystalline phase was detected in the XRD patterns. By comparing to the samples without coatings, electrochemical impedance measurements (EIS) made as a function of time suggested that the Li-Al hydrotalcite coatings act a good barrier from corrosion. To summarize, the Li-Al HT coatings prepared by the in situ growth technique shows great potential for the protection of Al alloys.

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Lin, J. K., & Uan, J. Y. (2009). Formation of Mg, Al-hydrotalcite conversion coating on Mg alloy in aqueous $HCO_3^-/CO_3^{2-}$and corresponding protection against corrosion by the coating. Corrosion Science, 51, 1181-1188.

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Bentonite in papermaking – complexity of interactions in colloidal systems of real life

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In the paper making process a lot of water is needed. Therefore many paper mills are historically located close to a river or the sea, in order to get fresh water from the river and get rid of the used water afterwards, too. Nowadays most paper mills produce paper products in huge factories with almost completely closed water loops. In these systems a lot of impurities accumulate, which may cause severe production issue after a while. In particular various substances of rather hydrophobic nature, derived from waste paper or wood extractives, agglomerate to tacky or sticky macroscopic particles, which may form deposits all over the paper machine or visible spots on the paper product itself.

Due to their enormously high available surface area in dispersion bentonite products are applied successfully for treatment of water loops in the paper industry since the seventies. High-quality bentonite products are very effective additives for cleaning of paper loop water, in particular for adsorption of colloidal-dispersed and fine-dispersed micro-particles.

From a scientific point of view, it is very difficult to investigate and understand in detail the various interactions of the adsorption- and flocculation-processes in such a complex system as the paper pulp or paper loop water, due to the fact, that the chemical nature of the many different ingredients, and the particles sizes and proportions of these different ingredients and a lot of other factors of influence like shear force, pH, temperature and other conditions may vary heavily over time and at different stage of the papermaking process. Therefore thorough scientific work is often neglected compared to empirical results of fast and simple methods applied in the paper industry.

S&B Industrial Minerals is a world-leading producer of bentonite products and also for the paper industry. As a lot of aspects of the interaction of smectites with other ingredients and components in the papermaking process haven't been fully understood in detail so far, there is plenty of room for fundamental research in this field of application.

Möbius C.H., Wochenblatt der Papierfabrikation 105, S. 733-740 (1977) Nr.18,
Möbius C.H., Wochenblatt der Papierfabrikation 105, S. 799-802 (1977) Nr.19
Möbius C.H., Wochenblatt der Papierfabrikation, S. 889 - 894 (1978) Nr. 23/24

Innovative clay sorbents for heavy metal immobilization

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Environmental pollution as well as impacts from natural processes lead to unwanted dispersion of metals in the biogeochemical cycle, thus requiring novel approaches for removal/decontamination of various types of pollutants. Clay is widespread resource and is used for diverse purposes from construction and production of ceramics to medicine and cosmetics. Clay in Latvia do have relatively old history and is of importance for further development of many applied products in order to seek for new approaches for the use of raw local resources. Within the present study clay samples of different geological genesis were chemically modified and tested with analytical methods. The modification approaches include chemical modification with organosilicon compounds as well as graft polymerization. Sorption of Pb, Cu, Ni, Zn and Cd by modified clay is based mainly on reactions of physical capture on complicated structured surface and ion exchange reactions. This is dominated by physical chemical properties and high sorption capacity of material. The modified clay products demonstrate significantly higher sorption capacities and properties supporting their applications for diverse purposes. Further areas of application of modified clays include their use in cosmetics and medicine.

Green rust and ferrihydrite-coated pozzolana as new filtration materials for water dephosphatation

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Thick green rust (GR) and ferrihydrite (Fh) coatings onto pozzolana (Pz) are demonstrated to be efficient phosphate sorbents. High iron quantity, up to 8.5 wt.%, can be deposited onto pozzolana when a “dry contact” method is optimized (Fig. 1a).The kinetic rate and sorption capacitiesin various experimental conditions (phosphate concentration, pH, …) are determined in “batch” tests. Predictions of breakthrough curves (BTC), obtainedunder different water velocitiesand column residence times, are developed from surface complexation modeling parameters derived from “batch” sorption data. Moreover, phosphate anions introduced into water withdrawn from a sewage treatment plant are fully adsorbed on the surface of this filtration material and a positive synergetic effect induced by soluble calcium species is observed (Fig 1.b).

The “Agence Nationale de la Recherche” project (ECOTECH2009 - N°0994C0103) is gratefully acknowledged for financial support.

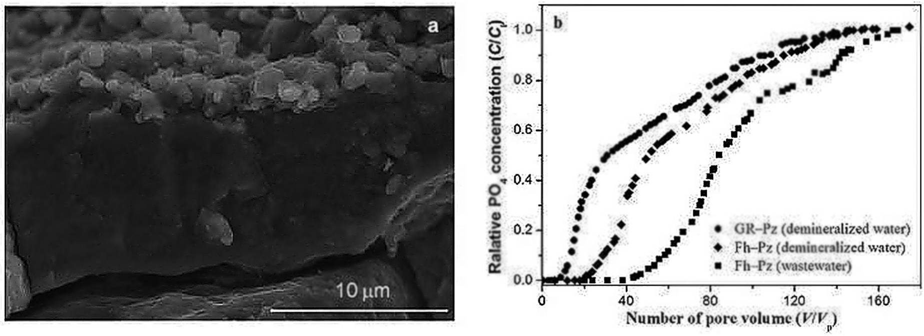

Figure 1. a) SEM image of thick GR coating onto Pz and b) BTC of phosphate ions for GR-Pz and Fh-Pz-packed columns at 0.5 mL min^{-1} flow rate.

Use of modified montmorillonite for the oxidation of aqueous sulfide

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Sulphur compounds are originated from industrial activities of man as well as from natural sources such as volcano eruptions, thermal springs and bogs. Concern for the environment and applicable regulations preclude the discharge of such sulfide-containing water to rivers, lakes or estuaries. For wastewater streams containing relatively large amounts of sulfides, it is conventional to contact them with acid and large amounts of steam to drive off, e.g., H2S gas. This gas is recovered and converted, to elemental sulfur. The implementation of this procedure is costly and became uneconomical when only small amounts of sulfur are present in relatively large currents. Consequently, there has been a considerable interest on developing efficient and low cost systems for the removal of sulfide from gas and aqueous phases. Among low-cost adsorbents Clay minerals present adsorptive properties and some modifications would improve them.

In this work, montmorillonite (Mt) was chemically modified by the addition of dextrose (Mt-Dex) or sucrose (Mt-Ac) and further thermal treatment at 180 ºC for 6 hs. For comparison effects, a commercial carbon was used as reference and Mt-Ac samples were prepared with different amounts of sucrose (from 25 to 90%). The modified Mt and the raw material were characterized by total surface, XRD and zeta potential determinations. The doped Mt shown three times higher sulfide oxidation capacity compared with the other materials. It seems that source of carbon used to dope the Mt, do not affect sulfide oxidation capacity. However the amount of carbon directly increases the sulfide oxidation capacity of the materials. An interesting feature of the samples doped with high amount of carbon is that after a few minutes of the start of reaction, the material becomes green (typical color of long polysulfide) which suggest that samples adsorbs the polysulfide from the solution with a reduction in the intensity of typical band. Zeta potential determinations of doped Mts showed less negative surface charge values than MMT. The XRD patterns for both Mt-Ac and Mt-Dex samples shift the d001 reflection 0.22 nm, respect to that of Mt, indicating the Carbon incorporation in the interlalyer. The chemical modification of the Mt by carbonization of sugar derivate introduced surface oxygen groups, which strongly improved the activity for sulfide oxidation

Bacterial removal of clay and iron minerals from quartz particles

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The mineralogical composition of fine fraction coating the surface of quartz particles always significantly affected the purification of quartz sands. Quartz sand occurs in varying degrees of purity in dependence on relation to mineral composition, but only a small percentage is suitable for glass industry after washing and magnetic separation treatment. In the case of the low quality of sand, voids of iron, and content of clay and silt could be observed. Most of the poorly ordered clay minerals agglomerates were encapsulated by iron oxide, which were impregnated in the quartz particle unsmooth surface. Experimental studies of the effect of bacteria on clay and iron removal were performed in either closed (batch) or open (percolated columns) reaction vessels. The influence of the biological leaching by heterotrophic bacteria on the process of quartz sands purification was evaluated by changes in the chemical composition of the clay fine sample before and after bioleaching. The extracted iron and clay products were characterized by XRD, FTIR, chemical and granulometric analyses, SEM and EDX. The iron-bacteria complexation by exudates caused the iron mineral dissolution. The bioleaching caused a break of the binding strength between iron and clays. Under static bioleaching conditions the initial oxygen content of 9 mg/l O_2 was consumed by microbial respiration within 2 days, indicating the formation of an anaerobic environment, which was suitable for bacterial iron dissolution in leachates to prevent iron oxidation and reversible contamination of quartz surface particles. This process of quartz sand bioleaching includes bacterial adhesion to the mineral surface of quartz particles and the targent production of organic acid into the iron-clay bonds of surface minerals, this because the pH decreased from 5 to 3.5 and the surface of the quartz particles was cleaned. It was confirmed, that the X-ray amorphous Fe oxides were dissoluted with the successive releasing of poorly ordered clay minerals from the surface of quartz particles, giving suitable purification results after the bioleaching of quartz sands.

This work was supported by the VEGA Agency supporting the project 2/0019/09 and PROJECTO CORFO I + D Cod. 13IDL2-23505.

Application of agarose-layered double hydroxide nanocomposite hydrogels as adsorbent

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Layered double hydroxides (LDHs) are a class of layered compounds, and are also called anionic clay. The most common group of LDHs can be represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}_{x/n} \cdot mH_2O]$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, A is an anion, and x usually ranges between 0.20 to 0.33. Anions in the interlayer space are exchangeable, and due to the anion exchange properties, LDHs are expected to be promising anion adsorbents.

In this study, as a new type of adsorbents using LDHs, agarose-LDH nanocomposite hydrogels were synthesized. First, aqueous colloidal LDH dispersion was prepared by a previously reported method [1]. The mixture of the colloidal LDH dispersion, agarose and water was boiled to dissolve the agarose. When the mixture was still hot, appropriate amount of water added again to adjust the agarose content to 1% of the total mass of the mixture, and then the mixture was cooled to room temperature to form a hydrogel. SEM observation revealed that LDH nanoplates were uniformly dispersed within the agarose polymer network. Ratios of LDH and agarose by weight varied from 25:100 to 200:100. The nanocomposite hydrogels were cut into small cubes about 3 mm to a side, and treated with an acetate-buffer/NaCl solution in order to eliminate carbonate anion contamination from CO_2 in the air and replace interlayer anions with Cl^- before adsorption tests. Because the hydrogels contained a large amount of water (>97%), the adsorption ability was evaluated by normalizing the amounts of adsorbed anions by Al contents in LDHs.

LDH nanoplates dispersed in the gels were expected to have large external surface areas, and it was also expected that anion adsorption would have increased especially in the case of anions that were not easily intercalated into the interlayer space. Results, however, showed no particular adsorption increase was observed. Nevertheless, when ratio of LDH and agarose increased to 1:1 or more, the adsorption ability of the gels was comparable to powder LDH. From this point, it was found that agarose can be used as a binder that has an interesting aspect that molding into various shapes is possible by using it.

This work was supported by JSPS KAKENHI Grant Number 24510115.

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Chromium removal using organo- and bio-montmorillonites

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Chromium is one of the most abundant inorganic groundwater contaminants at hazardous waste sites. Compared to Cr(III), the Cr (VI) forms chromate (CrO_4^{2-}) or hydrogen chromate ($HCrO_4^{-}$) that is more toxic and more soluble under different pHs and because of the negative charges, its adsorption on aquifer minerals is limited.

The conventional treatment of chromate-rich effluent is based on the reduction of Cr(VI) to Cr(III) and precipitate Cr(III) as chromium hydroxide, or chromium iron hydroxide at high pHs, resulting in a very expensive treatment. Clays are extensively used as low cost Cr adsorbents (Dimos et al., 2012). Recently an improvement in the Cr adsorption efficacy was indicated for surfactant treated montmorillonite or organo-montmorillonites (OMMT) (Kumar, et al, 2012).

In this work Cr(VI) adsorption was evaluated in: a raw MMT, a OMMT (exchanged with octadecyltrimetilammonium Bromide) and a bio-MMT (obtained by growing *Acremonium sp*), denoted O-MMT and Acre-MMT, respectively. The maximum adsorption for all samples was found at pH 3. The Chromium adsorption on O-MMT sample showed maximum adsorption at all pH respects to the other samples. At pH 3 the Cr adsorption value obtained for OMMT agree with data obtained by Kumar et al (2012).

The XRD analysis of MMT, O-MMT and bio-MMT samples indicated reflection peaks (001) values at 1.26, 2.12 and 1.24 nm, respectively. These data indicate that ODTMA enters as pseudotrilayers or paraffin-like monomolecular arrangements, while the fungi specie does not enter in the interlayer. The samples after Cr adsorption at pH 3 showed different behaviors of the reflection peaks (001): for MMT an enlargement was found while for O-MMT and bio-MMT samples not changes were found. In agreement with Kumar et al (2012) the apparition of new XRD peaks at 23.47 and 51.23 °(2θ) confirmed the Cr adsorption.

The negative Zeta potential values of MMT sample (-30 mV) was reduced after Cr adsorption, indicating a neutralization of the edge positive charges. For O-MMT sample the Cr adsorption diminished the positive charge of O-MMT sample from +20 to +15. While for bio-MMT sample no changes were found in the Zeta potential, remaining the Zeta potential values around -28 mV.

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Effect of hydration of bio-clay matrices on uranium adsorption – applications in upflow columns

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In previous studies, the generation and characterization of bio-clay matrices (BMMT) was efficient for the removal of U(VI) from aqueous solutions (Olivelli *et al.* 2013). Previous results indicated that dried BMMT presented an increase of the uranium adsorption capacity compared to wet systems. Previous results indicated that BMMT presented optimal characteristics for their use as bio-filters for the removal of U(VI) (Olivelli *et al.* 2012). The objective of this work is to study the causes of the increase in the adsorption capacity of dry BMMT and their use in U(VI) adsorption upflow columns.

Hydration rates of previously dried BMMT were determined. These percentages were correlated with the U(VI) adsorption ability of wet and dry systems and the mass of water that entered to the matrices during the rehydration process. Also, U(VI) adsorption capacity of dry, wet and rehydrated BMMT samples, were compared. Upflow adsorption columns using pellets of BMMT were performed. The effective diffusion coefficient (D_{eff}) was determined. BMMT showed diffusion coefficients comparable to those of natural clay. At dry bulk densities between 1.5 and 2 g/cm³ no influence on the diffusive transport regarding the surface changes by biopolymers could be detected.

The U(VI) adsorption capacity of rehydrated systems was similar to that found for wet systems. This may indicate that differences in the U(VI) adsorption capacity between the wet and dry samples were due to conformational changes that occurred during the drying process.

BMMT stability in columns depended on the biomass/MMT relationship; and this was optimized. Values of maximum adsorption capacity in columns were lower than adsorption capacity in batch systems. The effective diffusion coefficient increased with decreasing density for all samples.

BMMT presented an efficient adsorption performance for continuous adsorption processes; not only for its uranium retention high values (efficiencies up to 80%), but also they presented adequate stability of the material and the possibility of recovery.

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Mineralogical, grain-size exchangeable cations characterization of selected Portuguese clays – effects on viscosity behaviour

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Clays and clayey materials are used for a large range of applications, so it is very important to know their rheological, mineralogical and grain-size characteristics. Viscosity is an important parameter due to the widely use of clays in the ceramic industry, for example on ceramic tiles, in the chemical and pharmaceutical industries, among others applications (*Amorim et al., 2002*). Therefore, we considered important to study the viscosity of Portuguese clay suspensions and try to establish the relation with other parameters like mineralogy, grain size and exchangeable cations. For this assessment, clays from Portugal mainland and from Azores and Madeira islands were selected. Mineralogical characterization was performed by X-ray diffraction, grain size analysis was carried out by wet sieving for fraction >63 micra and by X-ray grain size analyzer (Micromeritics® Sedigraph 5100) for fraction <63 micra. Exchangeable cations were determinate by atomic absorption. Viscosity was determined using Brookfield DV-III Ultra Programmable apparatus. Results show that samples are mainly constituted by phyllosilicates and detrital tectossilicates like quartz and feldspars. Iron minerals are found also in some samples. More restricted is the presence of alunite, sulphur, pyrite and opal - CT which are associated mainly to volcanic materials. The most predominant clay minerals are smectite, illite and kaolinite. Grain-size results indicate that samples have variable amount of clay fraction (ranging between 13% and 89% of bulk granulometry). The predominant exchangeable cation is Ca. Viscosity results show us a correlation between some clay minerals (kaolinite and smectite) and with the amount of Ca and Na cations.

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This research was supported by Fundos FEDER through the Programa Operacional Factores de Competitividade - COMPETE and through the Fundos Nacionais através da FCT - Fundação para a Ciência e Tecnologia in the framework of the project “PEst-C/CTE/UI4035/2014”

Basic characterization of perlite from Lehôtka pod Brehmi deposit and its surrounds (Slovakia)

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Volcanic glass is an important initial material for origin of clay and zeolite minerals. However, volcanic glass is also significant raw material having unique properties. Perlite is hydrated acid volcanic (rhyolitic or rhyodacitic) glass with water content between 1 to 5% with characteristic onionskin texture and pearly luster. Major industrial utilization of the volcanic glass is in the form of expanded perlite, which is produced by quick heating (600-1200 °C; Šalát and Onšáková, 1964; Barker and Santini, 2006) of non-milled or grinded natural perlite.

In Slovakia occurrences of perlite are of economic importance but its utilization keeps behind the potential usage. Fundamental characterization of volcanic glass from perlite deposit Lehôtka pod Brehmi and its surrounds is an initial part of the project that should bring more profitable production of perlite through identification of perlite technological types. Lehôtka pod Brehmi perlite deposit is exploited from sixties. According to new findings the perlite deposit of the Sarmatian/Pannonian age is described as exogenous accumulation of perlitic breccia overlying early freatomagmatic pyroclastic rocks. Several perlite types form the breccia.

Quality of expanded perlite depends on technology of processing as well as qualitative parameters of raw perlite. Therefore following parameters are studied in the presented work: a) density and character of perlite cracks and porosity of volcanic glass by optical and scanning electron microscope; b) water content (mostly 3-5 wt%) and its type and binding by near-infrared spectroscopy and thermal analysis; c) amount of phenocrysts and microlites (mostly 4-7 wt%) in glass by optical microscope and X-ray powder diffraction; d) degree of devitrification by optical microscope.

The authors are grateful to the Slovak Research and Development Agency and VEGA for the support of the projects APVV-0339-12 and VEGA-02-162-11.

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Preparation of 2D optically active layers using beta-cyclodextrine/dyes supramolecular complexes

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The strategy for preparation of 2D-optically active layers based on hybrid organic-inorganic material based on supramolecular complexes was elaborated. The spectral behaviour and dye molecular orientation was investigated in the UV-Vis spectral range by the incorporation of dye molecules into thin montmorillonite films (MF). Cationic dye Pyronine and non-ionic dye Coumarine were used for modification of solid MF as single molecules and/or as supramolecular complexes prepared with b-cyclodextrin (CD) molecules. For detailed adsorption characterisation, equilibrium constants for supramolecular complex formation were determined from thermodynamic analysis. Successful adsorption of supramolecular complexes was proved by X-ray diffraction and by the inspection of the dichroic ratio of the prepared MF by UV-Vis spectroscopy. The molecular transition moments for dye monomeric species included in 2D MF of supramolecular complex for PY which absorbed at 560 nm were declined 60°. The Coumarine absorbing at 440 nm was declined 28° towards planar surface of MF. The angle and location of the Coumarine dye separated from the clay surface by the cyclodextrine rim seems to be favourable for the formation of J-aggregates with sufficient fluorescence intensity detected at 478 nm. This may enable utilisation of Coumarine type of dyes for the preparation of two-dimensional optical devices based on organic-inorganic hybrid materials.

Study of FRET in hybrid thin films based on saponite and cyanine dyes

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Fluorescence resonance energy transfer (FRET) in organized media has been a subject of many research works due to their potential applications in photochemistry. FRET is a physical phenomenon of the radiationless transmission of energy from a donor molecule to an acceptor molecule and leads to a reduction in the donor's fluorescence intensity and an increase in the acceptor's emission intensity. Intermolecular distance plays an important role in the course of the FRET. Preparation of hybrid systems based on layered silicates allows the suitable arrangement of chromophore's.

The main objective of present work was to prepare hybrid systems in both colloidal and thin films that exhibit the process of FRET. The hybrid systems were represented by cyanine dyes and smectites.

FRET was investigated between cyanine dye cations (N1, N2, N3) in colloids of layered silicate, synthetic Sumecton saponite. In these systems the dye molecules played role of the energy donors or energy acceptors or both. The adsorption and formation of various types of dye aggregates was studied using visible spectroscopy. The FRET process was described by fluorescence spectroscopy. Effects of various parameters on the efficiency of the FRET process, such as dye concentrations, saponite properties and the distances between co-adsorbed dye cations were found to be essential.

The preparation of thin films of saponite followed by the intercalation of the molecules of both- or three dye cations was performed in two ways. First way was the self-assembly process which is a simple method for the preparation of thin films and the second way was the layer by layer method, which allows the organized arrangement of the components.

Preparation of photoactive hybrid systems is a challenge due to the formation of non-fluorescent H-aggregates. This problem was solved by an appropriate modification of smectite with alkylammonium cations. Effects of alkylammonium cations with various chain length on the efficiency of FRET was studied. It was found that lenght of the carbon chain of surfactant cations played an important role in preventing the aggregation process.

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Nanoparticles of Fe_xO_y- palygorskite, efficient sorbates for pesticide removal

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Pollution of water resources with pesticides is a common environmental problem of growing concern in developing countries. Development of new materials with enhanced sorption ability of organic pollutants constitutes therefore a promising research field. The aim of the present work is to study the retention of traces of fenarimol in aqueous solutions using Algerian nanoparticles Fe_xO_y / palygorskite. These solids were synthesized by co- precipitation of both precursors from iron Fe^{2+} and Fe^{3+} in an alkaline medium to the fibrous support material.

Three samples of the Algerian palygorskite were studied: gross less than 90 microns “Atta@dz”, purified “P-Atta@dz” and amended with magnetic iron oxides “Fe_xO_y Atta@dz”. Different parameters, such as adsorbent mass, initial adsorbate concentration, reaction time and pH were optimized. Adsorption of the fungicide fenarimol was conducted using a “batch” system and fenarimol concentration remaining in the supernatant was determined by HPLC-DAD. Kinetic results show that the adsorption equilibrium was reached in several hours, more rapidly for Fe_xO_y -Atta@dz and Atta@dz than for P-Atta@dz. In all three cases the adsorption data were fitted to a pseudo-second order kinetic model. Adsorption isotherms indicated that adsorption rates of 70%, 50% and 11%, were reached for Fe_xO_y-Atta@dz, P-Atta@dz and Atta@dz, respectively.

The adsorption isotherms were modeled by Langmuir, Freundlich, Temkin and Dubinin - Radushkevich models to assess the sorption extent as well as to infer the mechanism of adsorption associated. The adjustment isotherms showed that our experimental results agree well with the models Langmuir, Temkin and Dubinin - Radushkevich.

The nanoparticles Fe_xO_y / palygorskite have proven their ability to retain fenarimol in aqueous solutions and could be used in future studies aimed at the reduction of environmental polluted areas.

Mineralogical and thermal properties of kaolinite deposits from Acoculco (Mexico)

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Kaolinite production of Mexico does not supply the needs of the country. Kaolinite deposits from Acoculco, Puebla, have been occasionally exploited but never characterised. work a characterization of kaolins from the Acoculco area is presented. These deposits occur in the Volcanic Caldera complex Tulancingo-Acoculco, between the northeastern part of the Trans-Mexican Volcanic Belt and the Sierra Madre Oriental provinces. Kaolinite was formed as a result of a strong hydrothermal alteration of alkaline-calcium volcanic sequences associated with episodes of intense magmatic activity of Miocene-Pleistocene age.

The chemical composition of major and trace elements was determined. Mineralogy was obtained by powder diffraction X-ray, infrarred spectroscopy and scanning electron microscopy. Thermal properties were determined by differential thermal analysis-thermal gravimetry (DTA -TG).

The Acoculco kaolins are mainly made of kaolinite, between 55 and 76 wt%, and about 27 wt% of. opal (Near this site, at Huayacocotla, kaolins contain about 70% of kaolinite and 5-10% of opal. They also contain tridymite (3-11 wt%), alunite (2-12 wt%), quartz (1-3 wt%) and gypsum (up to 3 wt%). The Fe_2O_3 content is low, between 0.09 and 0.17 w%. The Na_2O content is 0.02 - 0.18 wt% and K_2O is 0.07 - 0.16 wt%. In all cases, the heavy metals occur in low amounts, preventing environmental pollution at different stages of mining and processing.

DTA -TG of samples show an endothermic peak corresponding to the loss of the OH groups of kaolinite, at about 550 °C and the exothermic, at 990 °C, due to the crystallization of the mullite phase. Occasionally, a second endotherm appears at about 768 °C due to the decomposition of alunite. Water loss overlaps that of the OH groups of kaolinite. Dilatometric thermal evolution analyses of samples show a characteristic morphology with an initial shrinkage at about 550 °C due to the loss of the OH groups. A second shrinkage at around 850 °C corresponds to the collapse of the structure and the formation of metakaolinite. A third step at 1050 °C is linked to mullitization and the start of sintering. Some cases show a dilatation around 200 °C due to the α - β transformation of tridymite.

The diversity of applications of kaolin from Acoculco is hindered by its high silica content but favoured by its low iron and alkali.

Synthesis and characterization of taylor-made organo-clays for biotechnological applications

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The present study was aimed at the preparation and characterization of new tailor made hybrid materials, whose peculiar hosting capability towards different kind of molecules could be further exploited in several biotechnical application as well as oral drug administration or waste water remediation.

Kinetic and equilibrium studies on the Tween 20 uptake ability by K10-montmorillonite (MMT) have been carried out on varying some internal parameters, namely, pH, bio-surfactant concentration and Tween20/MMT ratio. The variation of these parameters allowed us to establish the role played by the hydrophilic/hydrophobic interactions in governing the adsorption process of the bio-surfactant onto the clay minerals.

The gathered kinetic data have been quantitatively analyzed by means of robust approach both for the non-linear regression and the subsequent residuals analysis in order to significantly improve the results in terms of precision and accuracy.

Classical and more complex models reported in the literature have been used.

The adsorption mechanism has been elucidated on the base of the complementary equilibrium and kinetic studies, then, corroborated by the useful information provided by the FT-IR and XRD characterization of the obtained composite materials.

The Tween20 adsorption onto MMT, at pH 1.0, takes place accordingly to two parallel reactions involving the neutral and the cationic form of the surfactant, which interact with two non- energetically equivalent binding sites of the clay surfaces, i.e. the interlayer region and the faces of the lamella.

Thermally activated clays as a main binder component for producing low-CO_2 concrete

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The manufacturing of ordinary Portland cement is characterized by high emissions of CO_2 and process temperatures of higher than 1300 °C. In recent years, there has been increasing interest in using of thermally activated clays (MetaClays) as a pozzolanic material to replace parts of the Portland cement.

MetaClays can be produced from clay raw materials (deficient in lime) by a thermal treatment at lower temperatures (550 °C – 950 °C), resulting in lower emissions of CO_2.

The aim of the investigations was to develop concrete cobblestones based on thermally activated clays as a main binder component. Six clay raw materials (containing kaolinite and illite in various proportions) were thermally treated at temperatures between 550 °C and 950 °C. The pozzolanic reactivity of the MetaClays was determined by using the standard chapelle test. The achieved reactivity was related to the type (kaolinite, illite) and the amount of the clay minerals in the raw materials. Metakaolin reveals the highest reaction potential and the widest temperature range of useful activation. However, the degree of activation of the illite clays can be enhanced by the technological parameters of the calcination.

Mortar prisms were produced with cements blended with different amounts of the MetaClays. Strength activity index was determined to evaluate the potential of thermally activated clays as a binder component. Lab-scale (laboratory oven, mortar prisms) and industrial-scale (rotary kiln, concrete factory) investigations have been made.

The thermally activated clays were able to substitute cement up to 60 wt.-%. Pre-cast concrete cobblestones based on MetaClays have been successfully produced. The higher the amount of kaolinite in the raw material the higher was the potential substitution level. However, illite clays are globally available in sufficient quantities. They offer a great potential as an alternative binder material.

The commercial bentonite from Kopernica (Tertiary, Slovakia) – petrographical and mineralogical approach

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The Kopernica bentonite deposit (Neogene) is located in Western Carpathians (south-western margin of the Kremnicke Vrchy Mts), in the Kremnica Volcano-Tectonic Graben (Central Slovakia Volcanic Field). The commercial bentonite from Kopernica deposit (BENOX s.r.o.) is currently used by CERTECH Company (Poland) to produce materials intended for zoological applications and other industrial sectors. It is thought that high-quality commercial bentonites should contain over 80% of montmorillonite, in order to ensure the desired properties of manufactured goods. However, the accessory minerals, which are present in bentonites in variable amounts, may influence their properties. The aim of this study is the assessment of the Kopernica bentonite phase composition and surface properties based on petrographical and mineralogical studies. The commercial Kopernica bentonite (three samples) in natural state and separated into <2, 2-63, and >63 µm size fractions was studied. The XRD analyses show that the material consists of montmorillonite, quartz, opal C, micas, potassium feldspar, plagioclases and zeolite. The thin section petrography revealed that the rocks studied have fragmented, eutaxitic texture. They are composed of collapsed pumice fragments into lenticular masses (fiamme), which are strongly deformed and altered, but good retention of the shard structures is visible. The compressed glass shards are molded around crystal fragments such as quartz, biotite and zonal plagioclase. The FESEM/BS studies display that the axes of the shards and the walls of the flattened vacuoles are outlined by the inward-growing microlites of silica (axiolitic texture), whilst the interiors of the shards are altered to clay. The devitrification also occurs around isolated nuclei to form spherulites composed of silica and zeolite. The authors argue that the presence and form of occurrence of non-clay components such as zeolite and opal C strongly influence the surface properties of the Kopernica commercial bentonite.

Funding partially provided by the Grant no 11.11.140.319 of the AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Kraków, Poland.

Hydrotalcite/montmorillonite nanocomposite

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The work aimed at synthesis of a composite material built of exfoliated/delaminated anionic clay mineral of hydrotalcite type and exfoliated/delaminated cationic clay mineral of montmorillonite type.

Ca-exchanged form of montmorillonite (Jelšovy Potok, Slovakia) and a synthetic magnesium-aluminium hydrotalcite (Mg:Al=2) were used for the synthesis. Both minerals were transformed into organic derivatives by ion exchange with decyltrimethyl ammonium cation (DTMA) in the case of montmorillonite and dodecyl sulphate anion (DDS) in the case of hydrotalcite. This step aimed at an increase of the interlayer distance and hydrophobization of the solids, to facilitate swelling in an organic medium. Both organo-derivatives were subjected to treatment with 1-octanol at 70 °C, aided by ultrasonication, to promote exfoliation/delamination. Suspension of montmorillonite transformed into an iridescent solution, and that of hydrotalcite formed a clear solution. Restacking could be induced by addition of acetone. Composite material was synthesized by mixing the colloidal solutions of delaminated minerals, ultrasonication and 16 h treatment at 180 °C in a microwave mineralizer. The resulting transluscent solution was treated with acetone to cause precipitation of the solid composite.

Physico-chemical characterization with XRD, XRF, FTIR, SEM, TG/DTG/DSC confirmed that the ion-exchange of starting minerals with organic species did occur. Recovery of delaminated montmorillonite from octanol solution resulted in a solid with structure similar to that observed in the starting material, while the interlayer space of restacked hydrotalcite was 10% smaller than in the initial sample. XRD analysis of composite precipitated from mixture of delaminated mineral organo-derivatives revealed the presence of reflections characteristic of montmorillonite and absence of features attributable to hydrotalcite. Simultaneously, SEM/EDS analysis confirmed the presence of Mg and Al in the same proportion as in the starting hydrotalcite. The results indicate that the composite may be envisaged as built of an organo-montmorillonite particles mixed intimately with dispersed hydrotalcite layers.

The work was financed by NCN project OPUS 2013/09/B/ST5/00983 and AGH project nr 11.11.140.319.

Properties and processes at the aqueous interface of clay minerals

Water at interfaces – the potential effect of water structure on charging phenomena

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Various examples of mineral-electrolyte solution interfaces exist, where the behavior of particles and single crystals turns out to differ a lot.

In particular the isoelectric point of single crystal samples is found to be unexpectedly low compared to the concomitant (nano)- particles.

The phenomenon is explained by the structuring of water at smooth surfaces. In particular hexagonal surface structures (also found on the basal planes of many clay related minerals) appear to favor the presence of a water film that causes nominally hydrophilic surfaces to finally expose a hydrophobic surface.

On such hydrophobic surfaces (encompassing diamond, ice, oil, or Teflon) unexpected pH-dependent charging has been experimentally observed for a very long time.

Currently, only the assumption that hydroxide ions are strongly attracted by these hydrophobic surfaces can explain both the observed pH dependence and the negative charge at pH >4 for all these systems.

Our hypothesis is that on the smooth hydrophilic substrates with appropriate surface structure, water films generate properties that are similar to those of hydrophobic substrates. Measurable properties like surface forces or zeta-potentials on single crystals of sapphire or hematite basal planes are reminiscent of the results obtained on the inert surfaces.

Roughness generates perturbations of the water film and inhibits the hydrophobic properties. Ice nucleators like clay particles or silver halides are affected by these phenomena.

Our own experimental data are set into this context and we use published molecular dynamics simulations and vibrational spectroscopy results to link between macroscopic measurements and molecular scale information.

The conclusion is that smooth single crystal samples best suited for several spectroscopic methods are probably not ideal analogues to study the structure and bonding of contaminants in natural systems.

Cation diffusion in the interlayer space of swelling clay minerals – a combined macroscopic and microscopic study

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Diffusion is the main transport process occurring in geological systems characterized by low hydraulic permeability, as shales and engineered barriers considered for the storage of nuclear wastes. Such environments are generally rich in swelling clay minerals, in which water and solutes can diffuse in interlayer spaces. In the framework to constrain models predicting diffusion in porous media rich in swelling clays, this study aims at investigating the specific diffusion of calcium cations confined in the interlayer space of 5 mm sized disks of vermiculite during the Na-for-Ca exchange process. Vermiculite material was chosen as model swelling clay because this mineral does not present any osmotic swelling in water saturated conditions, as compared to low-charge montmorillonite generally considered in literature.

Diffusion experiments are performed at four different NaCl salinities (3.10^{-3}, 5.10^{-2}, 0.1 and 1 M) of the exchanger solution. Macroscopic analysis of the diffusion process, based on the analysis of the aqueous calcium concentrations released in solution, is performed using a pore diffusion model, classically considered in literature. When decreasing salinity of the solution, the effective diffusion coefficients obtained for calcium are found to increase up to values higher than self-diffusion coefficient of calcium in bulk aqueous solution. Furthermore, the apparent interlayer calcium diffusion coefficients interpreting chemical calcium profiles in the disks decreases with both NaCl salinity and diffusion time. A set of molecular and brownian dynamics simulations is used to quantitatively interpret the evolution of macroscopic diffusion coefficients with experimental conditions. The close agreement obtained between microscopic simulations and macroscopic experimental data allow us to quantitatively determine that the dynamical properties of calcium is driven by both the external gradient between the solid and the solution related to the salinity of the solution, but also by the internal calcium/sodium gradient in the solid as a function of the diffusion time. These findings should contribute to the improvement of pore diffusion models used to describe the diffusion of cations/pollutants in compacted swelling clay minerals.

Ion exchange of major inorganic cations (Na, K, Ca, Mg, H) on beidellite – experimental and modeling approach

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Reactive transport models are generally used to predict the fate in time and space of contaminants after the closure of mining sites. In this context, species which are adsorbed onto minerals constitutive of the rocks and which are easily release in pore water of the system (exchanged species) have to be predicted with good confidence. In the context of a uranium mining site in Kazakhstan, smectite characterized by a tetrahedral charge (beidellite) appeared to be the main phase which could be involved in ion-exchange reactions. As only few data are available in literature concerning ion-exchange reactions occurring on smectites with tetrahedral charge, this present study is devoted to propose an ion exchange model able to describe experimental sorption isotherms obtained for different couples of cations on a beidellite. As major cations are always strong competitors of metallic cations for clays, Na/H, Na/K, Na/Ca and Na/Mg ion-exchange isotherms were performed on a Na-saturated beidellite (<0.3 µm; SBDId1). Experimental isotherms were interpreted according to one-site and three site models based onto the Gaines Thomas convention, and the three sites approach allowed to propose selectivity coefficients considering a constant total sorption site density equal to the cation exchange capacity of the sample.

This model was applied to predict the evolution of beidellite surface composition toward major inorganic cations in context of uranium mining site remediation. Results were compared with outputs of a three site model based on bibliographical data for montmorillonite (smectite with octahedral charge). An effect of the localization of the charge of the smectite (for the same total foliar charge) was evidenced.

The ion-exchange model proposed for beideillite allowing to interpret different experimental sorption isotherms involved proton and major cations of naturals waters (Na^+, Ca^{2+}, Mg^{2+} and K^+) could be included in reactive transport models and is valid for Cl total normality $>10^{-3}$ mol/L, pH ranging from 1 to 7 and for aqueous concentrations ranging from 10^{-3} to 10^{-1} mol/L. This model could be used for a better understanding of ion-exchange reactions occurring in many environments where beidellite is present: from soils to deep sandstone or shale formations.

Cs^+-for-Na^+ exchange on vermiculite – influence of particle size

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Caesium has been released in environment after several accidents in nuclear power plants (e.g., Fukushima in 2011 and Chernobyl in 1989). Due to the high solubility of this element in natural waters, caesium is mainly present in its cationic Cs^+ form in subsurface environments, particularly in soils. Moreover, as a result of the reactivity of swelling clay minerals towards cations, caesium mobility in soil strongly depends on the content of these minerals, such as vermiculite. For this reason, selectivity coefficients are needed to describe the cation exchange process between Cs^+ and major cations, as Na^+, on vermiculite. Only few thermodynamic constants relative to the sorption of Cs^+ on vermiculite have already been proposed in literature. However, the validity of such thermodynamic constants remains questionable, as the Cs^+ sorption on high-charge swelling clays, as vermiculite, may not be fully reversible. Moreover, the nature of the sites involved in such a reversible sorption process, is not clearly identified.

In this study, Na^+/Cs^+ sorption isotherms were obtained on three distinct size fractions of vermiculite (0.1-0.2; 1.0-2.0 and 10-20 mm, Reinholdt et al., 2013), displaying contrasted lateral, basal and interlayer specific surface areas. To assess the contribution of interlayer sites in the overall sorption process, X-ray diffraction profile modelling procedure (Tertre et al., 2011) was applied on the samples obtained along the Cs^+-for-Na^+ sorption isotherm.

For each size fraction, the results showed that the cation exchange capacity strongly decreased when the amount of Cs^+ sorbed on the solid increased. In addition, the sorption site density involved in the reversible part of the exchange process increases with the decrease of particle size. This could likely be attributed to the increase of lateral sites. By contrast, the irreversible Cs^+-for-Na^+ exchange in the interlayer sites was attributed to the low hydration state of Cs^+ cation, which limits the diffusion of this species in the interlayer space of vermiculite. Molecular Dynamic simulations are planned to derive the self-diffusion coefficients of Cs^+ and Na^+ in the interlayer of vermiculite in order to assess this hypothesis.

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Tertre, E. et al. (2011). *J. Coll. Interf. Sci. 363*, 334-347.

The interaction between bentonite and water vapor

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The influence of water vapor on bentonites or smectites respectively is of great interest in many different fields of applied mineralogy like nuclear waste sealing or casting in foundry industry. The vapor affects the smectite surface and perhaps its structure, which leads probably to a change of its properties in a mostly unfavorable way. Therefore the influence of water vapor (200 °C) on some properties of smectite-group minerals has been studied. Turbidity, sedimentation volume, XRD, XPS, methylene blue sorption, water adsorption, cation exchange capacity, aspect ratio, isoconductive point, dynamic mobility and viscosity were measured on both untreated and treated samples. Only few physico-chemical and mineralogical parameters caused differences between vapor-treated and raw samples. As shown by XRD and XPS, the crystalline structure of smectite remained unaffected by vapor. Also equivalent sphere diameters were not systematically modified. Differences in CEC between unprocessed and treated samples were observed, but only for smectites with monovalent interlayer cations. Changes of CEC and methylene blue sorption kinetics indicated a modification of charge conditions at the smectite surface. Changes in swelling capacity or sedimentation volume triggered by water vapor are also related to surface charge modifications. As shown by Bish et al. (1997) changes of contact angles and zeta potentials delivered a further proof for apparent modifications of surface properties by water vapor. From the experience of physico-chemical and mineralogical measurements the bentonite species plays a minor role, whereas interlayer cation and its valence respectively is of greater importance. Aspect ratio and isoconductive point, derived from conductometric titrations, alter due to the steam treatment. Dynamic mobility and viscosity are also influenced by water vapor, but only for samples with a monovalent interlayer cation.

The conclusion from above presented measurements is that due to the steam treatment the surface conductivity of smectite particles changes, depending on the interlayer cation.

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Preparation and characterization of kaolinite nanostructures

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Kaolinite nanostructures and nanohybrids play an increasing role in our life as possible additives and packing materials, surface coatings or catalysts. Nanostructures can be obtained by stepwise intercalation. Complete delamination of the kaolinite structure can be achieved via multiple intercalation with adequate reagents. Morphological changes accompanying delamination are influenced by several parameters.

In this work, nanostructures of pseudo-hexagonal and tubular (halloysite-like) morphology were synthetized from kaolinites with varying structural order. Potassium-acetate as intercalation reagent was used in the first step, followed by treatments with ethylene-glycol and hexyl-amine reagents to ensure total delamination. The morphology of the delaminated structure depends on the crystallinity of kaolinite, the conditions of precursor synthesis and the way of energy transfer. Surface properties and morphology show a significant correlation. Surface properties (specific surface area, pore size distribution) were measured by N_2 adsorption, while inverse gas chromatography (IGC) was used to quantify surface energy and acid-base properties. It was found that IGC is a useful method for the surface characterization of clays providing data necessary for the preparation of nanohybrids with tailored surface properties.

This research was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the frame of the TÁMOP 4.2.4. A/2-11-1-2012-0001 ‘National Excellence Program’ and TÁMOP-4.2.2/A-11/1/KONV-2012-0071 projects.

Influence of particle size and mineralogy on edge sites reactivity of montmorillonite

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Montmorillonite properties are mainly responsible for bentonite behaviour, and especially interfacial interaction with their environment involving water binding and/or trace element sorption capacity. In order to assess the bentonite performance and predict/control the long-term bentonite behaviour a fundamental understanding of montmorillonite properties is pre-requisite. The montmorillonite mineral general characteristics, structural and chemical heterogeneities are well-known (Emmerich et al., 2009 and references herein). The layer charge properties and the resulting cation exchange capacity behaviour were thoroughly studied in particular by Maes et al. (1979), Wolters et al. (2009), Kaufhold et al. (2011, 2013). However, correlation with morphological parameters was restricted to a few samples (Tournassat et al., 2003), although "edge to face" surface area ratio is a fundamental parameter for their reactivity.

Four purified and Na-saturated montmorillonites <0.2 µm separated from technical bentonites from different locations were characterized in particular by their structural composition, layer charge and specific surface area in this study. Statistical AFM measurements on single layers were performed to determine particle size distribution and aspect ratio of these 2:1 layers. Based on the geometrical parameters, the variable charges at the particle edges were estimated according to Tournassat et al. (2003). Then, the variable charges were compared to CEC measurement (Cu-trien method) on reduced-charge montmorillonites (Li-exchanged montmorillonite followed by heating at 300 °C) (Hofmann-Klemen effect). Good agreement of the different techniques applied was obtained and the influence of particle size distribution on mineral properties and surface processes will be discussed in the presentation.

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Wolters, F. et al. (2009). Clay Clay Miner 57(1): 115-133.

Acid leaching of Fe-riched clays – effect on adsorption properties

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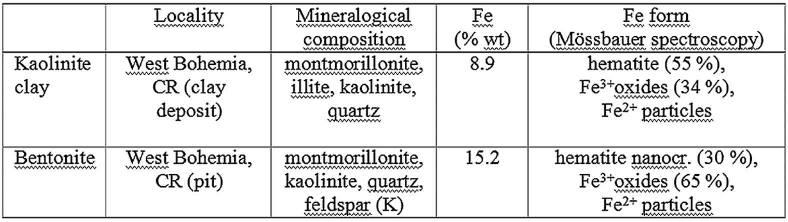
Iron bound in clays does not participate in sorption processes. However, Fe released and phase-transformed by the acid leaching can take part in surface reactions and form complexes and/or covalent bonds via Fe ions. Two Fe-rich clays (Tab. 1) were treated in 0.5 MHCl (pH = 1.1) and 0.15 M$(COOH)_2$ (pH = 1.2), and then used for the adsorption of As(V)/Sb(V) oxyanions from model solutions. Adsorption efficiencies of raw and acid-treated samples are summarized in Fig. 1. Equilibrium sorption capacities q_{max} increased from 2.3×10^{-3} to 39.2×10^{-3} mmol g^{-1} for As(V) and from 2.4×10^{-3} to 40.1×10^{-3} mmol g^{-1} for Sb(V). The leaching in 0.5M HCl enhanced both As(V) and Sb(V) adsorption, the leaching in 15 M $(COOH)_2$ improved Sb(V) adsorption only. Bentonite containing less crystallic Fe forms proved better sorption properties for both oxyanions. The leaching of Fe ran according to the first order kinetics, while the adsorption of As(V)/Sb(V) according to the second order kinetics.

This work was the part of the project 13-24155S (Grant Agency of Czech Republic).



	Locality	Mineralogical composition	Fe (% wt)	Fe form (Mössbauer spectroscopy)
Kaolinite clay	West Bohemia, CR (clay deposit)	montmorillonite, illite, kaolinite, quartz	8.9	hematite (55 %), Fe^{3+}oxides (34 %), Fe^{2+} particles
Bentonite	West Bohemia, CR (pit)	montmorillonite, kaolinite, quartz, feldspar (K)	15.2	hematite nanocr. (30 %), Fe^{3+}oxides (65 %), Fe^{2+} particles

Figure 1. Characterization of clay samples

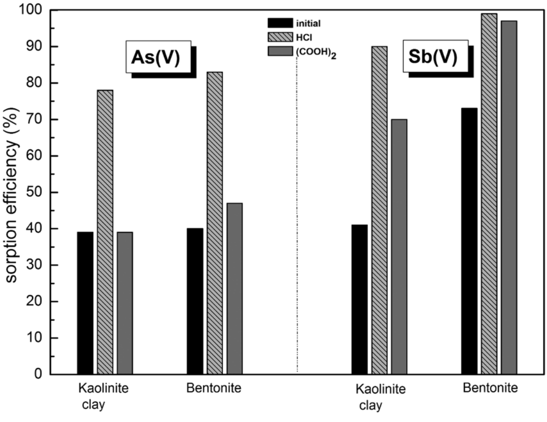


Figure 2. Adsorption efficiency of raw and acid-treated clays

Preparation and photochemical application of kaolinite-silver nanocomposites

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Layer-structured minerals are especially suitable for the immobilization of nano-particles on the surface or in the interlamellar gallery. The nanohybrids thus formed represent improved adsorption and catalytic properties. Nanohybrids with catalytic properties are of utmost importance in the light of their potential use in the preparation of self-cleaning surfaces, surface coatings/layers.

The photocatalytic efficiency of the generally used TiO_2 (anatase) is reduced by the quick recombination of the (e+-h-) pairs upon UV irradiation. The recombination of the e+-h- pairs can be significantly reduced by Ag nanoparticles prepared onto the surface of TiO_2 due to the Schottky barrier formed at the metal - semiconductor interface. Due to its low specific surface area, TiO_2 has a low adsorption capability. The specific surface area, the rate and extent of adsorption as well as the photocatalytic activity can be increased with the use of suitable supports, e.g. clay minerals.

Silver nanoparticles were prepared onto a delaminated natural kaolinite containing 0.6 w/w% TiO_2 from a 0.5 M $AgNO_3$ solution via UV irradiation for 12, 24 and 48 h. The photochemical activity of the surface was followed by FTIR spectroscopy through the decomposition of benzenesulphonic acid as a test compound in the presence of (5-4-dimethyl-amino-benzylidene)rhodanine upon exposure to a 254 nm UV light for 20, 40 and 60 minutes. These experiments were carried out with the untreated mineral, as well. It was found that the delaminated mineral itself has a photocatalytic activity (due to its TiO_2 content) if rhodanine is present on the surface. Independently of the irradiation time, only the acid is decomposed when the pristine mineral was used. With the delaminated mineral, however, rhodanine is decomposed, as well.

This work was supported by the European Union in the frame of the TÁMOP-4.2.2/A-11/1/KONV-2012-0071 and TÁMOP 4.2.4. A/2-11-1-2012-0001projects.

Sorption and desorption of soluble organic matter in Boom Clay

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In Belgium, the Boom Clay (BC) is studied as a potential host rock for a deep geological repository for nuclear waste because of, among others, its low water permeability and good retention capacity toward radionuclides. However, BC contains also a significant amount of organic matter, from 1 to 5 wt%, with 50 to 200 mgC/L found dissolved in pore water. Although the influence of dissolved organic matter (DOM) on radionuclide mobility has been proven in many occasions, the mechanism controlling the amount of soluble organic compounds in pore water, and their interaction (sorption, leaching) with the solid phase have not been clearly identified. These mechanisms are particularly important to predict the evolution of the amount of DOM in pore water over time.

In this presentation we aim to bring together the current knowledge regarding the processes which control the DOM concentration in Boom Clay porewater, with particular focus on the effect of clay minerals and pore water chemistry.

In this purpose, sequential leaching experiments on Boom Clay samples are currently ongoing. Two different set of experiments are performed. In a first set, leaching experiments are conducted on rock samples with variable content of clays minerals in order to evaluate the role played by clay minerals in the interactions of soluble OM with BC. These experiments are carried out with synthetic clay water solution and in Ar/CO_2 0.4 ppm atmosphere to mimic as much as possible *in situ* conditions. In a second set, a clay-rich BC sample is used with the same atmosphere but the chemistry of the leaching solution varies. This allows evaluating the effect of pore water chemistry on soluble OM-BC interactions. Solutions with variable pH and ionic strength are considered. Different salt are also used, NaCl and $CaCl_2$, to estimate the involvement of cation bridging mechanism.

Desorption kinetics was followed during the first step and reveal that dissolution of soluble OM is not instantaneous and that kinetically-controlled mechanisms are involved.

Several empirical models including linear and non-linear sorption equilibriums and non-equilibrium sorption with kinetically-controlled desorption or diffusion process from particles matrices will be applied to the experimental data.

Following the sequential leaching experiments, sorption experiments are performed with DOM extracted from Boom Clay. Results of leaching and sorption experiments will be confronted to determinate the reversibility of the sorption processes.

Sorption efficiency of selected metals on kaolinites grafted with aminoalcohols

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Removal of toxic and/or carcinogenic ions from aqueous media is of environmental importance. Kaolin group minerals exhibit relatively low sorption capacity. Their surface charge results mainly from protonation/deprotonation phenomena taking place at the particle edges influenced by the pH. Moreover, in contrast to 2:1 layered clay minerals the migration of ions into their interlayer space is not possible. Recently it was shown that an appropriate functionalization improves the sorption of selected oxyanions (Matusik and Bajda, 2013, Matusik, 2014). The chemical treatment usually involves grafting with organic molecules which enables the access of ions to the interlayer space. Moreover, most importantly the grafted materials are resistant to water washing. The research objective was to examine the sorption behaviour of kaolinite-based derivatives towards Pb(II), Cd(II), Zn(II), Cu(II), Ni(II), and Cr(III).

The Polish kaolinites from: Maria III deposit (M) and Rusko-Jaroszów deposit (J) were used for the study. The M and J were modified through interlayer, high temperature grafting of diethanolamine (DEA) and triethanolamine (TEA) using DMSO intercalates as precursors. The new materials structure was characterized by XRD and FTIR. The sorption was tested both in equilibrium (concentration range: 0.005-10.0 mmol/L) and kinetic studies (0.5-20 min) in single- and multi- element systems with cations concentration measured by AAS method.

The sorption capacity of grafted kaolinites showed an increase as compared to the raw kaolinites which was more visible for the J-based derivatives. The sorption improvement was due to migration of cations into the interlayer space and their subsequent chelation by amine nitrogen. The most significant sorption improvement both in single- and multi- element systems was observed for the Cu(II) ions which readily form complexes with N-donor DEA and TEA molecules. The sorption isotherms in most cases were in agreement with the Langmuir model and the kinetics followed the pseudo-second order model.

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Matusik, J., Bajda, T. (2013) J. Colloid Interface Sci., 398, 74.

This project was supported by the Polish National Science Centre under research project awarded by decision No. DEC-2011/01/D/ST10/06814.

Adsorption of tiabendazole on organically modified montmorillonite.

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Water contamination by fungicides is a significant problem that has been solved for years. A possible way of water decontamination in agricultural regions is using organically modified clay. We calculated the structure of interlayer space of Wyoming montmorillonite (Wy-MMT) intercalated with octadecyltrimethylammonium cations (ODTMA) and the adsorption of tiabendazole molecule (TBZ) on Wy-MMT and on Wy-MMT intercalated by ODTMA (Wy-ODTMA).

The results of modeling showed a parallel orientation of ODTMA with respect to the MMT layers, ODTMA cations are horizontally shifted with respect to each other and the shift equals approximately to a half of ODTMA chain. We obtained a few possible basal spacings (1.94 nm, 2.00 nm and 2.10 nm) with a small difference of total energy. It is in qualitative agreement with experimental findings, where a mixture of two basal spacings was observed (ca 2.0 and 2.1 nm). The calculations of adsorption of TBZ molecule on Wy-MMT and on Wy-ODTMA surface showed that TBZ molecule interacts mainly via electrostatic interactions with sodium cations located in hexagonal cavities of MMT layer. The adsorption energy of TBZ between Wy-MMT and Wy-ODTMA is very similar and is of about -50 kcal/mol. If TBZ molecule is adsorbed together with ODTMA cations on the Wy-ODTMA surface the adsorption energy ranges from -10 kcal/mol to -5 kcal/mol. The differences in adsorption energy confirm experimental measurements where in case of Wy-ODTMA the desorption of TBZ was of 83% while in case of Wy-MMT no TBZ desorption was observed.

Adsorption of Indigo Carmine from aqueous solution onto montmorillonite using full factorial design

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Effluent from the textile industry is loaded of non-biodegradable dyes which make them difficult to apply biological treatments (Tahir and Rauf, 2006). Several techniques have been employed to remove dyes from wastewater; adsorption is being the most used actually. The indigo carmine (IC) dye was used as a model for aqueous systems because, now a day, great quantities of dye residues are discarded by textile industries in the environment (Cestari et al., 2008; Abu-Eishah, 2008). A 2^3 factorial design was employed to evaluate the quantitative removal of the indigo carmine dye from aqueous solutions on montmorillonite. The variables were chitosan masses of 1,00 and 10,00 g, IC concentrations of 20 and 200 mg/L and pH of 3 and 7. The surface analysis techniques were applied to better understand the spatial composites structure and posterior evaluate the different aspects of the dye adsorption process into the clay composites, associated with the results from the adsorption isotherm experiments (Zhu et al, 2013). The constants in the Freundlich, Langmuir and Temkin isotherms were calculated (Wang et al, 2005). The factorial design required the execution of a relatively small number of different experiments (Bingöl et al, 2010). To determine the statistical significance of the effects, duplicate determinations were made for each of these experiments to evaluate experimental error.

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The impact of EC and pH on the the adsorption of Zn and Cd by palygorskite mineral

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In this study, a natural palygorskite clay from (Dogtown, FloridaUSA) was selected as an adsorbent, and the adsorption capacity of Cd (II) and Zn (II) onto the adsorbent was investigated. The effects of parameters such as EC, pH of suspension solution, and amount of particle size of the adsorbent on adsorption capacity for Cd (II) and Zn (II) were studied. To understand the adsorption mechanism, the variation of the pH and EC ($S \cdot m^{-1}$) of the Cd (II) and Zn (II) solution in the adsorption process and the different adsorption models that can describe the adsorption of Cd (II) and Zn (II)) onto natural palygorskite were determined.

The effects of various experimental parameters were investigated using a batch adsorptiontechnique. Adsorption of Cd and Zn by pure palyorskite as a function of pH (pH 6, 8 and 10), EC (EC 4, 6 and 8) and the amount of Cd added range from 0-100 mg/L to this mineral were studied. The shape of the isotherm were L1 and L2 type isotherm for the sorption of Zn (II) and L2 type isotherm only for the sorption of Cd (II). The basic mechanism governs the Cd adsorption characteristics of palygorskite at studied pH is adsorption and ionic exchange. However, for Zn (II) the adsorption on the pure palygorskite show similar trend as Cd at low pH and EC but at high pH values the adsorption of Zn was minmal comparing with Cd suggesting a precipitation. The results were fitted to both the Langmuir and Freundlich isotherms. Satisfactory agreement between experimental data and the model-predicted values was expressed by the correlation coefficient (R^2). The fitness of the adsorption data of the adsorption of Cd and Zn on palygorskite into the Freundlich isotherm confirmed its heterogeneous nature. Data from this study proved that metal cations from aqueous solution can be adsorbed successfully in significant amounts by palygorskite.

Electrokinetic potentials, surface conductivity and cation exchange capacities from the electrical conductivity of kaolinite suspensions

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Judged by the number of publications on the electrochemical properties of clay mineral-aqueous solution interfaces, the interest in electrokinetic potentials and related parameters is high. Closer inspection of published accounts shows that there are only two contributions (Rowlands and O'Brien, 1995 and Rasumssen et al., 1997) which provide reasonable estimates of electrokinetic potentials. This is due to the almost ubiquitous neglect of surface conductance and the non-sphericity of most clay minerals.

In this work results from conductivity experiments on kaolinite suspensions are presented. We used the theoretical descriptions of O'Brien and Ward (1988) to calculate electrokinetic potentials by taking into account the non-spherical particle shape and surface conductance originating behind and beyond the shear plane. Having then electrokinetic potentials available, ionic components of the diffuse surface charge density were calculated which permit the estimation of cation exchange capacities. The c.e.c's calculated in this way compare favourably well to c.e.c's usually observed for kaolinites.

Using the theoretical formalism of Dukhin and Derjaguin (1974), aspect ratios can be estimated from the conductivity of suspensions as well (Weber et al., 2014), which enables us to solve the necessary equations without the use of any adjustable parameter.

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Removal of chromate, arsenate and phosphate oxyanions by halloysite from Dunino deposit, Poland

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The highly mobile, soluble ionic forms of Cr(VI) and As(V) are toxic and/or carcinogenic. The excessive amounts of these oxyanions including P(V) may cause serious health problems and adverse environmental issues e.g. euthrophication. Halloysite is a dioctahedral 1:1 layered kaolinite polytype characterized by a high stacking disorder. The sorption properties of halloysite are governed by surface charge which is mainly due to protonation/deprotonation effect taking place at the particle edges. Recently it was shown that functionalization of kaolin group minerals improves the sorption of selected oxyanions (Matusik and Bajda, 2013, Matusik, 2014). Interestingly, the anions removal by pure halloysite was relatively high without any chemical treatment. Thus, a detailed study of the sorption behaviour of natural halloysite in reactions with Cr(VI), As(V), and P(V) was carried out.

The halloysite from Polish Dunino deposit (H) owned by the Intermark Company was selected for the study. The Dunino deposit was formed due to basalt weathering. The mineral sample consists of dehydrated, nanotubular halloysite-7 Å and platey kaolinite in 60:40 ratio as estimated by the formamide test. Additionally, minor amounts of Fe-minerals are present i.e. magnetite and ilmenite. The specific surface area S_{BET} and total pore volume V_{TOT} are equal to 49.5 m^2/g and 0.28 cm^3/g, respectively. The sorption was tested in equilibrium studies in single- and multi- element systems. The Cr(VI), As(V), and P(V) sorption capacity measured at initial pH 5 was equal to ~20 mmol/L, ~160 mmol/L, and ~200 mmol/L, respectively. The affinity of halloysite surface towards Cr(VI) was relatively low. On the other hand the As(V) and P(V) uptake was very high and comparable to modified zeolites and smectites (Mozgawa et al. 2011). This was due to efficient surface complexation of As(V) and P(V). In multi-element systems the P(V) was sorbed preferentially.

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Matusik, J., Bajda, T. (2013) J. Colloid Interface Sci., 398, 74.
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This project was supported by the Polish National Science Centre under research project awarded by decision No. DEC-2011/01/D/ST10/06814.

Interactions of clay-based pigments with organic binders

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Clay-based materials represent a large group of artistic pigments of natural origin, the so-called “earthy pigments”. The identification of individual clay minerals in paintings is difficult because the samples are usually very small (less than 1 mm), heterogeneous, and pigments are mixed with organic binders. Some clay minerals (e.g. smectites and mixed-layered structures) react with these binders and form organo-clay complexes. We simulated these interactions in laboratory conditions using model mixtures of smectites or mixed-layered illite/smectite structures with most typical organic binders (skin glue, linseed oil, egg yolk). Interplanar distance of smectites increases after the interaction with aqueous solution of skin glue, while with linseed oil and egg yolk it decreases. The changed values remain stable after the drying of samples. Mixed-layered structures behave as mechanical mixture during the interactions. The results were used to reconstruct the hypothetic unmodified structure of original clay minerals used in historical paintings before the interaction with the binder. It helped us to differentiate clay-based materials of various origins, which is an important parameter in provenance studies of artworks.

Hybrid material based of kaolinite and rhodamine B

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Hybrids based on organic and inorganic components include a broad spectrum of the materials with variable structures, properties and functionalities. These materials include also hybrid systems composed from clay minerals with adsorbed fluorescent dyes. Such materials have mostly been prepared from smectites via ion-exchange reactions. Material based on rhodamine dye covalently bound to kaolinite surface is introduced in this presentation. The hybrid was preparedby the reaction of reactive silane molecules bearing rhodamine moieties with hydroxyl groups on kaolinite surface. The mineral was pre-expanded with dimethylsulfoxide (DMSO), which enabled a relatively large fraction of its surface to be accessible for the modification. The swelling of kaolinite and its intercalation with the dye were investigated by X-ray diffraction. The intercalation brought about disordering of kaolinite structure. Covalently bound dye moieties were resistant to a mild thermal treatment. Photophysical properties of the hybrids were studied by UV-vis absorption, steady-state and time-resolved fluorescence spectroscopies. Covalent anchoring of the fluorophores groups on the surface partially prevented dye molecular aggregation. However, it required only small concentrations of the adsorbed dye to keep its photoactivity. Only small fraction of the molecular aggregates was found by the methods of fluorescence spectroscopy. Majority of the adsorbed dye exhibited a relatively high photoactivity leading to fluorescence quantum yield comparable to the values found for rhodamine solutions. The modification of kaolinite with covalently bound fluorophores may expand mineral's applications to new industrial fields.

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0291-11 and Grant Agency VEGA (2/0107/13, 1/0943/13).

The role of clay minerals in the metal sorption in soils as studied by analytical transmission electron microscopy

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Soil mineral phases play a significant role in controlling trace metals mobility and availability in soils through adsorption-desorption processes. In this study, batch Cu and Pb sorption experiments on soils with contrasting characteristics were combined with the complex mineralogical study of the metal-sorbed solid phase by XRD, TEM-EDS and FT-IR spectroscopy. Our aims were to study the metal sorption capacity of individual soil mineral phases and to evaluate the effect of presence of mineral phases affecting the sorption capacity of soil particles, such as iron oxides and carbonates.

Lead could be characterized by higher and stronger sorption on the studied soil samples when compared to Cu. As long as Pb was preferentially associated to soil organic matter Cu sorbed mostly on soil mineral constituents. Additionally, the competitive situation resulted in increase of the role of iron oxide phases in Pb sorption. Among soil mineral phases, highest metal amounts were immobilized on the swelling clay mineral particles (smectite, vermiculite), but iron oxides may also have similarly high sorption capacity for Pb. The close association of iron oxides and silicates resulted in significant change in their sorption capacities for all the studied metals generating sorption capacity to also phase which otherwise do not adsorb metals. Alkaline conditions due to the carbonate content in the studied samples resulted in both increased role of precipitation for the studied metals and in elevated sorption capacity for Cu by discrete mineral particles which was not found for Pb.

Using the analytical transmission electron microscopy analyses, the sorption characteristics of metals onto soil mineral phases could be supported by particular data. When the methods used in this study are combined, they become an extremely powerful means of getting a deeper insight into the soil-metal interaction.

This study was financially supported by the Hungarian Scientific Research Fund (OTKA K105009).

A study of phosphate removal by calcium-iron layered double hydroxydes

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Ca^{II}-Fe^{III} layered double hydroxides (LDHs) were synthesized by three ways of coprecipitation method, from both chloride and nitrate salts and with x varying from 0.2 and 0.33 (x is the Fe^{III} molar fraction), to evaluate the phosphate removal effectiveness from aqueous solution. The pristine LDHs were characterized by X-ray diffraction (XRD) and Raman spectroscopy (Fig.1) and the phosphate anions removal mechanism was studied by coupling results of analytical (kinetics, isotherms, pH effect …) and spectroscopic analyses.

The maximum phosphate uptake capacities at pH = 7 are obtained from LDHs with x = 0.25 prepared by adding dropwise the cationic solution into a NaOH solution. Moreover, the chloride intercalated Ca-Fe LDH seems to be more efficient than the LDH with intercalated nitrate anions, as the maximum capacities are 570 and 496 mg g^{-1} respectively. Anyway, all studied LDHs show excellent results compared to iron oxides. Indeed, phosphate adsorption capacities never exceed 100 mg g^{-1} for iron oxides [1].

[1] K. Barthélémy et al., J. Colloid Interface Sci. 384 (2012) 121.

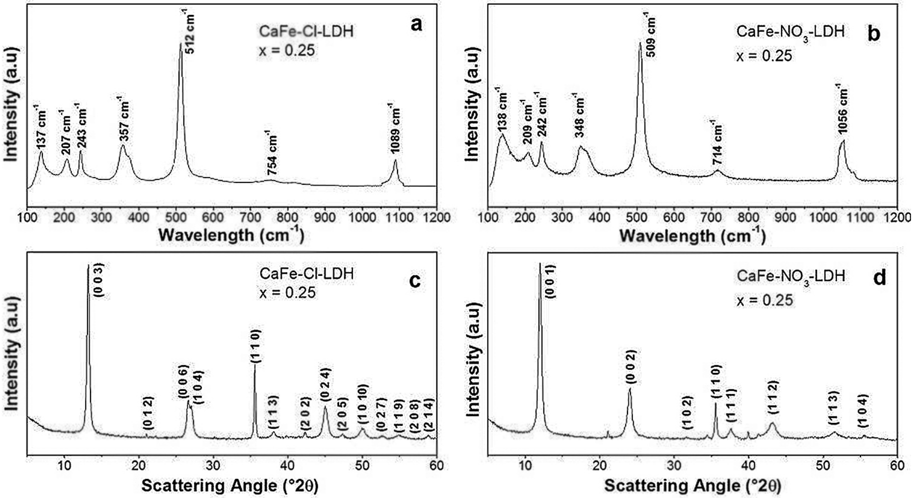

Figure 1. Raman spectra (a and b) and XRD patterns (c and d) of pristine LDHs

Comparison of interactions between montmorillonite surface and organic species

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Montmorillonites (MMT) type Wyoming and Cheto due to their enormous surface area and extendable interlayer space can be used as effective adsorbents for various organic species. Montmorillonite is used in its natural or modified form. Modified form means host layers intercalated by various organic cations. The resultant properties of materials with various adsorbents are very different (originally hydrophilic surface turns into hydrophobic after sorption of organic compounds, changes in fluorescence properties, etc). The adsorption of ammonium cations, aromatic compounds like phenol, aniline and dyes cations was studied and mutual interactions between these organic species and host layer were compared. Modified montmorillonites were prepared by the intercalation and the sorption of quaternary tetramethylammonium salts (TMA) into the interlayer space and with various cations or polar molecules on the surface of MMT.

The experimental and calculation results revealed that intercalated montmorillonites adsorbed phenol much more readily than the pure sample (even though phenol was apparently more adsorbed into the interlayer space in the case of pure MMT). Aniline adsorbed itself strongly on MMT; while using the TMA intercalates (TMA-MMT), its adsorption decreased. The modelling results revealed the important role of water forming a moderately concentrated layer on the pure MMT surface. Water molecules enable the adsorption of aniline on MMT and, on the contrary, repel phenol molecules from MMT. In the case of TMA-MMT, lower amount of water near a silicate layer caused decrease in the aniline adsorption and, on the contrary, increase in the phenol adsorption. In case of dyes, they should be only adsorbed on the surface of motmorillonite for increasing photoluminiscence properties of materials. Intercalated dyes with various arrangements do not show evident influence for photoluminiscence properties. Decreasing of layer charge and prevent intercalation lead to significant decrease of mutual interactions between layer and dyes and on the other hand higher by several orders of magnitude photoluminiscence. The surface models were studied in detail by techniques of molecular simulations in Material Studio modelling environment.

Zeta potential and antimicrobial activity of biodegradable chitosan/bentonite nanocomposite

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Various polymer/clay composites can be synthesized via different preparation methods, including polymer intercalation into the layers of clays, in which clay minerals are situated offer a variety of advantages such as high thermal stability, enhanced reinforcement, small particle size, layer expanding capabilities and insolubility [1,2]. Zeta (ζ)-potential measurements are very useful technique which provides information about the material surface-solution interface and colloidal stability of dispersed particles in a suspension. In this study, biodegradable chitosan (Cs)/bentonite(Bnt) nanocomposites with three different compositions were synthesized by the intercalation method using a cationic surfactant. The Cs/Bnt nanocomposites were characterized using conductivity, density, particle size measurements, FTIR, TGA, XRD and SEM methods. The characterization results revealed that there was a strong interaction between chitosan and bentonite units. Zeta potential of Cs/Bnt nanocomposite dispersions was examined as a function of time, pH, electrolytes, various surfactants, and temperature in aqueous medium. ζ-potential of the nanocomposites was observed to change in accordance with the clay content. The Cs/Bnt nanocomposites were also tested against various bacterial and fungal strains [3]. It was found that the antimicrobial activity of Cs/Bnt nanocomposites increased with an increase of clay content.

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Particle size and shape analysis of clays using electron microscopy

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The determination of clay particle size/shape is of utmost importance in understanding the physical and mechanical properties of clays and clay nanocomposites. Despite technical advances, particle size/shape analysis of clays remains a challenge due to artifacts of dehydration. This paper presents a unique technique of studying clay particles and their assembly in the natural state.

A special wet environmental-cell (EC) sample holder allowing *in*-*situ* observation of dispersed individual clay particles in a liquid environment was built. Bentonite clays collected from different localities were purified and dispersed in de-ionized water without any dispersion agent. Prior to fractionation, the cation exchange population was changed using NaCl solution and washing. Different size fractions (<0.2 mm and 0.2 to 2 mm) of the Na-exchanged bentonites were collected by the settling (pipet) method, and were examined in an environmental wet-cell TEM (WETEM). Traditional air-dried and cryo-TEM methods were also completed for comparison purposes.

The use of WETEM has led to the discovery of new shapes of nano-size smectitic clays. Clay particle size analysis revealed that almost all of the smectite particles were <500 nm in equivalent diameter with a mode between 30 to 125 nm and a mean between 90 to 180 nm regardless of the clay fraction obtained by settling method. Other techniques yielded thickness ranging from 4 to 10 nm, with the mode of 5 to 6 nm corresponding to about 4 to 5 unit cells. These values are slightly larger than those determined for pure Na-exchanged bentonites using colloidal chemical observations based on viscosity and light-transmission measurements [1]. This difference may have resulted from differences in dilution of clay minerals in the suspensions. With advanced hard and softwares, surface 3D images and 3D tomography can be constructed from images obtained from SEM, TEM and FIB. The application of 3D analysis of clays and its assembly promises to increase our understanding and improve the application of clays in many aspects.

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Adsorbtion of cadmium, chromium and lead cations on north-patagonic clay minerals

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Some physicochemical properties related to the adsorption behavior of a bentonite (CATAE) and two common clay minerals (named DTN2 and DTN3) from Cinco Saltos (North-Patagonia, Argentina) were characterized. Cation exchange capacity, exchangeable cations, specific surface area, surface charge density, permanent and pH-dependent charges, point of zero charge, isoelectric point and the elemental composition were determined.

Sorption and desorption experiments using Cd^{2+}, Cr^{3+} and Pb^{2+} solutions were carried out. To assess the monometal and multicationic adsorptions, batch equilibrium experiments using raw and purified materials, in aqueous solution at 298 K, pH=3.5 and at different ionic strengths were performed. Desorption processes by simple and successive extractions, with solutions of HCl and HNO_3 (0.1%) were performed. In all cases, the quantification of the metal ion remaining in solution was determined by atomic emission spectrometry (ICP-AES).

CATAE adsorbed significantly higher amounts of metal ionic species than common clays for equal sorption time. The adsorption of each metal ion was greater when the clay minerals were free of accompanying impurities. The retention rates were: 100% for Cr and Pb ionic species and 96% for Cd ionic species when CATAE is free of oxides and oxohydroxides of Fe and $CO_3^{=}$.

The affinities sequence for monometal adsorption was $Cr^{3+}>Cd^{2+}>Pb^{2+}$. Although the adsorption process was slower when ions compete for the same active sites the sequence remained when the multicationic solution was tested. HNO_3 (0.1%) soluction was more effective than HCl (0.1%) solution in the removal of most metal ions. For common clays the differences between the two acid solutions were not significant, although it should be noted that metal ions were more readily desorbed from common clays than CATAE. The desorption process changed when an inert electrolyte was added to the multicationic solution. Thus, for a solution containing 0.1 M KNO_3 both acid solutions removed 100% of Cd^{2+}, but only 2% of retained Cr^{3+} was desorbed, while for Pb^{2+} the percentage desorbed was 78%.

Two surface adsorption mechanisms were dominant, formation of outer-sphere complexes on basal surfaces and internal sphere complexes on edge sites.

CATAE showed high effectiveness in removing Cd, Cr and Pb ions from aqueous solutions.

Using of Fe-modified kaolines for decontamination of areas polluted by toxic oxyanions (As, Sb, Se)

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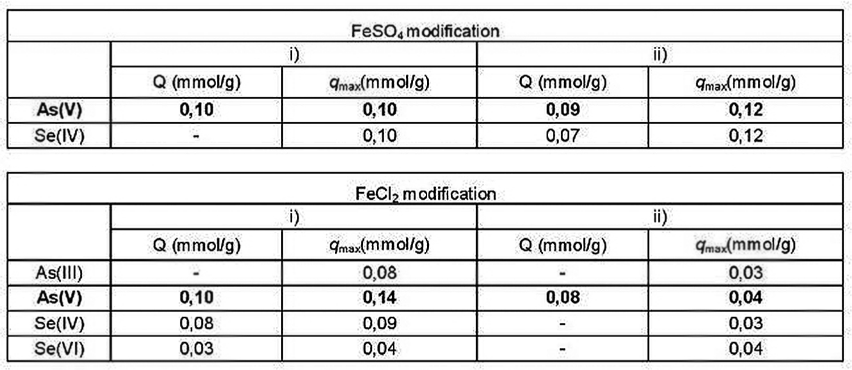
Natural clay materials are considered effective and perspective sorbents for economical and ecological reasons. In general, aluminosilicates are not selective sorbents for anionic contaminants thanks to a low pH(ZPC). Their simple surface pre-treatment with Fe^{II} can significantly change the surface charge and thus strongly improve the affinity to anionic contaminants.

This work deals with a sorption of toxic arsenic, antimony and selenium oxyanions on Fe-modified, calcinated kaolin with the use of two modification methods: i) The natural kaolin calcinated at 550 °C was treated by rehydration in autoclave with 0,6 Msolution of $FeCl_2$/$FeSO_4$; ii) The same kaolin calcined at 550 °C was agitated with 0,6 M $FeCl_2$/$FeSO_4$ (20 $g.L^{-1}$) in a sealed polyethylene bottle at ambient temperature for 24 hours. The concentration of initial As/Sb/Se solutions was 2.10^{-4} M.

The comparison of optimal adsorption parameters according to the Langmuir model is summarized in Table 1.

This work was the part of the project 13-24155S (Grant Agency of Czech Republic).



$FeSO_4$ modification				
	i)		ii)	
	Q (mmol/g)	q_{max}(mmol/g)	Q (mmol/g)	q_{max}(mmol/g)
As(V)	**0,10**	**0,10**	**0,09**	**0,12**
Se(IV)	-	0,10	0,07	0,12

$FeCl_2$ modification				
	i)		ii)	
	Q (mmol/g)	q_{max}(mmol/g)	Q (mmol/g)	q_{max}(mmol/g)
As(III)	-	0,08	-	0,03
As(V)	**0,10**	**0,14**	**0,08**	**0,04**
Se(IV)	0,08	0,09	-	0,03
Se(VI)	0,03	0,04	-	0,04

Figure 1. Theoretical and maximum adsorption capacities for i) and ii) modifications

Using of synthetic aluminosilicates for removal phosphates from aqueous environment

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The topic of this research is using synthetic aluminosilicates (hydroxisodalite, zeolit A and nalsite) for adsorption of phosphates from contaminated systems. Aluminosilicates generally demonstrate a cationactive behaviour in aqueous systems at pH >3.5. However, a simple pre-treatment with Fe^{II} salts (0.6 M and 0.3 M $FeSO_4/FeCl_2$) can significantly improve their sorption affinity to oxyanions, including phosphates. This modifications causes the presence of Fe^{2+}/Fe^{3+} oxyhydr(oxides) on the sorbent surface. The reasearch contained the measurement of adsorption series with Fe-modified sorbents to obtain theoretical parameters of sorption processes. The theoretical adsorption capacities according to the Langmuir model varied from 0,8 to 12,7 g.g^{-1}. The modification od hydroxisodalite with 0.6 M $FeSO_4$ was found as the most effective for PO_4^{3-} removal. The adsorption experiments ran at pH ≈ 7,5 and laboratory temperature in the bath manner.

This work was the part of the project 13-24155S (Grant Agency of Czech Republic).

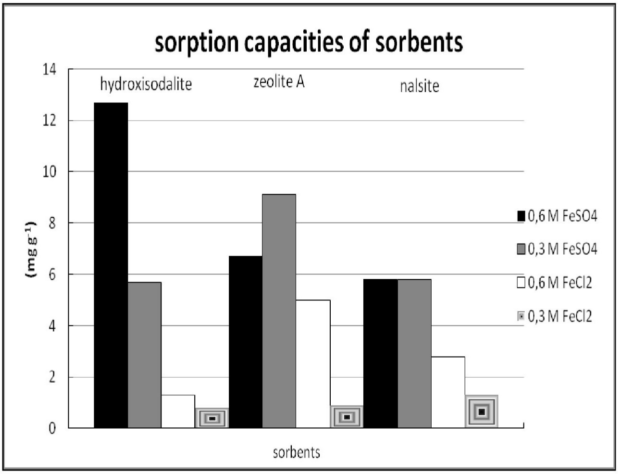

Figure 1. Optimal equilibrium sorption capacities

Effect of cyclic wetting and drying on swelling and non-swelling clay minerals

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Previous studies on metal-ion adsorbed smectites demonstrated that numerous (100-140) subsequent wetting and drying (WD) has significant effect on various properties of smectites. The most conspicuous change during WD cycles in the case of metal-adsorbed swelling clays is the decrease of crystallite size (both lateral dimension and thickness of clay platelets). As a continuation of the research begun, smectites with different layer charge and with naturally occurring interlayer cations (Na^+, Ca^{2+}, K^+), as well as various non-swelling phyllosilicates, clay minerals (kaolinites, muscovite, pyrophyllite, chlorite) were studied in order to answer whether WD cycles has similar effects on all kind of clay minerals. Mineralogical cheracteristics were determined by XRD, TEM, thermal analysis, FTIR and by sorption experiments.

After 120-140 WD cycles the basal reflection of Na-montmorillonites becomes broader, indicating the decrease of crystallite size. In the case of low charged montmorillonite, the basal spacing slightly increases with the number of WD cycles, suggesting some chemical modification. Na-smectites do not loss their expansion capacity during WD cycles, but their XRD patterns show degradation of the crystals. Ca- and K-saturated high charged montmorillonite does not show similar features. Basal reflection of K-smectite tend to decrease to 10 Å with WD cycles and it lose its expansion capacity. Due to potassium fixation cyclic WD significantly decreases the lead adsorption capacity of K-smectite, but does not influence remarkably the uptake by the same clay mineral when it is Ca-saturated. Adsorbed and interlayer water content of K-smectite also decreases during WD cycles. Non-swelling clay minerals behave otherwise: they do not show considerable decrease of crystallite size nor even after 240 WD cycles.

Results suggest that cyclic WD modify only swelling clay minerals, which can incorporate water in the interlayer space, however, it has no significant effect on non-swelling clay minerals. These changes may influence the chemical and physical properties of the soils or clay liners.

This research was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP 4.2.4. A/1-11-1-2012-0001 ‘National Excellence Program’.

Evolution of rheological properties of sodium montmorillonite dispersions near the sol-gel transition point

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Solid content as well as electrolyte concentration dramatically influence the structure type of montmorillonite dispersions. The structure can vary from separated sols to strong gels with different particle interactions. Depending on the salt content (NaCl) in water slow or rapid coagulation in sols leading to the formation of loose or compacted aggregates with different fractal dimension will occur. Gels formed near critical solid and electrolyte concentration possess different mechanical properties and thixotropic behavior. Samples were investigated by rotational viscosimetry using a Polymer RPE-1M viscosimeter and a Brookfield R/S plus rheometer in the shear rate and shear stress controlled regimes. In the shear rate controlled regime all dispersions show some solid-like behavior with some yield points, but in the stress-controlled regimes better differentiation between solid-like and liquid like systems could be found.

Structure formation and gel destruction were investigated near static and dynamic yield points and a hierarchical structure was shown to exist in water dispersion.

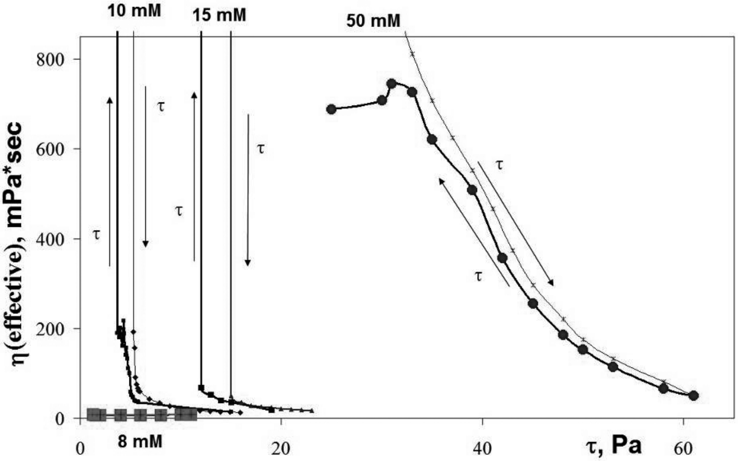

Figure 1. Consistency curves of 2.4% sodium montmorillonite. Blue curves - ascending viscosity dependence from shear stress, black descending

Influence of bentonite on sorption of organic compounds in groundwater aquifer

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The organic compounds contaminating groundwater are during their transport influenced by diverse factors. One of the most important factor is the sorption ability of these organic compounds on the clay minerals. In presented work the process of the sorption was investigated by laboratory batch as well as dynamic column experiments. Bentonite was used as the model solid phase and benzene, o-xylene, aniline and benzoic acid were used as a test compounds. The study of the kinetics of the sorption showed that the sorption rate in its primary phase could be described by the first order kinetics however, the second order kinetics was more suitable for description of the whole sorption process until the steady state. In the steady state the sorption rate was controlled by pore diffusion. It was found that for non-polar compounds the rate coefficient decreased as follows: o-xylene > toulene > benzene. The increasing concentration of bentonite in solid phase increased the sorption constant for phenol, o-xylene and aniline, while for benzene, toulene and benzoic acid only small influence was observed. The distribution coefficients (K_d = 1.5-200 l/kg) of particular test compounds decreased as follows: benzoic acid > phenol > o-xylene > aniline > toulene > benzene. The interactions between bentonite surface and test compounds were based on Coulomb forces when the partial charges on the substituent played the active role. The decrease of the pH value increased the sorption capacity of bentonite towards all test compounds except for benzene. The second order sorption rate constant of the test compounds was indirectly proportional to their solubility. The comparison of the results obtained from batch and dynamic experiments showed no substantial differences therefore, for the practical purposes it is possible to employ the results from batch experiments.

Kaolinites – ordering-disordering and adsorption properties

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Kaolinite group minerals have a similar chemical composition and at the same time a wide variety of structures. Most of the kaolinite and halloysite structural features can be described with a suit of methods such as XRD, SEM, IRS and DSC analysis. However, distinction of highly defective kaolinite and 7Å-halloysite is usually difficult. Vacancy displacements, layer rotation and its distortion within a unit structure lead to formation of many different defects both in the layer structure and their stacking. Detailed investigations of the kaolinites structure can help to study such important quality as its high absorptivity and to shed the light on the nature of this process for kaolinites. The aim of this research was to find out the influence of the kaolinite structural features on their adsorption properties.

Ten samples of clay fraction (Thus, we can distinguish possible defects arrangements in studied samples into three groups: 1) stacking faults of ordered layers; 2) stacking faults of defective layers; 3) ordered stacking of defective layers.

Adsorption properties were investigated by measuring the methylene blue adsorption kinetics with UV-vis spectroscopy. Also the vapour adsorption kinetics were studied with new proprietary equipment [1]. For all sample groups new experimental data were received. Using the data on kinetics of water vapour adsorption it was possible to obtain classic adsorption isotherms which turned out to be characteristic for kaolinites however the method is nonconventional. In its turn the kinetics graphs happened to be useful after mathematical processing. Logarithmical transformation of graphs allowed us to distinguish three different processes occurring during adsorption. Each of these processes was recognized as adsorption on different sites on mineral surfaces.

1. Artemov V.G., Kapralov P.O., Kurmasheva D.M., Tihonov V.I., Volkov A.A. Laser analyzer of water molecules interaction kinetics with an adsorbent // Instruments and experimental techniques, 2013, No 5, 117-121 pp.

Stability of engineered clay barriers in radioactive waste disposal

Clays and shales as long-term barriers for flow and contaminant transport

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The spectrum of clay-rich rocks that are studied in the framework of deep geological disposal for radioactive waste ranges from soft clays (e.g. Boom Clay in Belgium [porosity n = 0.37]) to moderately indurated units (e.g. Callovo-Oxfordian in France [n = 0.18], Opalinus Clay in Switzerland [n = 0.12]) and indurated shales (e.g. Palaeozoic units in southern Ontario, Canada [n = 0.07]). Smectite is typically abundant in the soft clays, whereas illite/smectite mixed layers account for the swelling capacity of the more strongly indurated formations. From the perspective of waste confinement, the key features of clays and shales include the low hydraulic conductivity and therefore the predominance of slow diffusive transport of contaminants in pore water, the self-sealing capacity of fractures and the retardation of migrating solutes by sorption. All these features are related to the characteristics of clay minerals and to the nanometric architecture of the pore space.

The clay-mineral spectrum in a shale formation provides information on sediment source, depositional environment and diagenetic processes. In contrast, pore waters residing in the pore space in most cases lack connate components and constitute archives of processes that occurred after compaction. A suite of techniques have recently been developed to extract pore waters from shales, both from core samples and in situ from borehole intervals. The pore-water composition is controlled by equilibria with minerals and by the chemical composition of ground waters in the embedding aquifers. The aquifer compositions may change over time due to geological processes such as marine transgression or emergence from the sea. Such changes in the boundary condition lead to diffusive fluxes in the shale pore water, and characteristic diffusion profiles may develop. If the spatial distribution of pore-water compositions in the shale is known, the diffusive fluxes can be reconstructed by transport modelling, providing constraints on the large-scale solute-transport behaviour in shales over geological periods of time.

Role of clay minerals on the carbonate chemistry in a marine clay formation

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Samples from different levels of the Opalinus clay formation at Benken were studied for their mineralogy using X-ray diffraction, and for chemistry of diagenetic calcite, using X-Ray diffraction and electron microprobe (EPMA). X-ray diffraction data combined with EPMA mean chemical composition of calcite indicate that the calcite *c* lattice parameter decreases with the decreasing Ca occupancy in its cationic site, and consequently with incorporation of trace elements in calcite, the major ones being Fe and Mg. At the scale of the formation, the trace element content in calcite is anticorrelated with clay content in the claystone.

The different generations of diagenetic calcite identified in a sample (micrite in clay matrix, and sparite in silty layers or lenses) exhibit almost the same trace element content, but are characterized by different Fe/(Fe+Mg) atomic ratios : <0.45 for micrite and ~0.7 for sparite. These data suggest that clay minerals have a constant control on the cation content of porewater from which calcite precipitated, but cation ratios are respected independently of cation sorption on clay minerals.

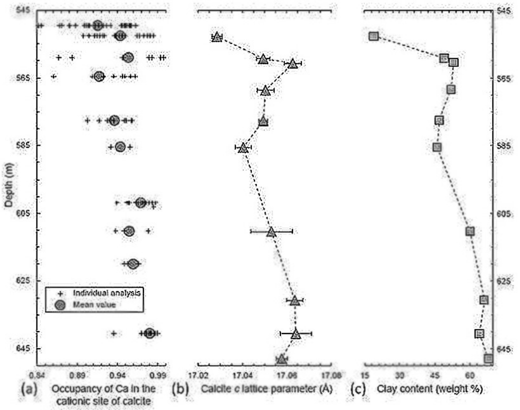

Figure 1. Evolution with depth of (a) Ca occupancy in the cationic site of calcite (determined using EPMA, each cross is an individual measurement, solid circle is the mean value of all values from a same depth), (b) calcite c lattice parameter (determined from refinement of calcite Bragg peak positions in XRD patterns) and (c) clay content (determined from quantitative refinement of XRD patterns and chemical data)

Monitoring and modelling the behavior of a high pH waters injected in an equipped borehole of the Meuse Haute Marne Underground Research Laboratory

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Since July 2010, Andra is conducting an in situ experiment within the Meuse Haute Marne Underground Research Laboratory. High pH (pH= 13.5) cementitious water is circulating in a chamber (75 cm height, diameter 76 mm) in an equipped borehole drilled in the GED gallery. Since the beginning of the experiment, the injected water has been renewed 4 times. Samplings are performed as a function of times and the gathered solutions are then analyzed. Major cations and anions are monitored with time as well as pH and alkalinity. D_2O has been also injected as a tracer. Iodine and bromide have been spike in the cementitious synthetic solutions to quantify the anions accessible porosity. In order to reproduce the pH decrease, the major ions changes within the solution a coupled geochemistry transport model has been built using PHREEQC. The transports parameters (diffusion coefficient, porosity, size of the zone around the borehole disturbed mechanically by drilling and equipement) have been calibrated on the D_2O data. Regarding the setting up of the geochemical reaction the tested models integrate multicomponent diffusion (MCD) and diffuse double layer effects in clays in conjunction with ion exchange and a full mineral assemblage has been taken into account. The results indicate that the K and Na evolution as a function of time is driven by the exchange on the clay. Taking into account the full mineral assemblage and allowing precipitation and dissolution of the minerals allow to properly reproducing the Ca profile over time. Introduction of dissolution kinetic allows a better representation of the pH decrease. Change of the transport properties as a function of time link to mineral dissolution/precipitation will also be discussed. At last but not least to which extend this results can be integrated in long term modeling experiment in order to predict the stability of engineered clay barriers in radioactive waste disposal will also be evaluated.

Montmorillonite as barrier material for uranium (VI) at high ionic strengths

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Clay and clay minerals are potential host rocks for nuclear waste disposal due to their high sorption capacities and low permeability. Thus far, research of radionuclide retention by clays has been focused on low ionic strength systems. The present work addresses North German clay deposits whose groundwaters show ionic strengths up to 4 mol/l in depths relevant for nuclear waste disposal.[1] The experimental set-up is modelled on conditions found in the Konrad mine, which serves as reference site. Montmorillonite is used as model clay for uranium sorption and diffusion experiments in sodium and calcium chloride as well as in a mixed electrolyte that resembles the groundwater at the Konrad site.

Ionic strengths effects, where sorption decreases with increasing ionic strength, can generally only be observed in the acidic pH range because they depend on cation exchange. Natural groundwaters at the Konrad site have pH values >5.5, where cation exchange has ceased to be the predominant sorption mechanism for U(VI), which in turn diminishes ionic strength influence. The sorption maxima in different salt systems lie slightly below the neutral point and within the pH range of groundwaters of the reference site. When approaching the ionic strength of North German groundwaters, sorption becomes partly irreversible.[2] Furthermore, uranium retention greatly increases with ionic strength in the alkaline pH range in the calcium chloride system. Both effects are attributed to secondary phase formation, which is promoted by increasing ionic strength. Additionally, spectroscopic results and surface complexation modelling of the system will be presented.

[1] Brewitz, W. et al. (1982) Eignungsprüfung der Schachtanlage Konrad für die Endlagerung radioaktiver Abfälle. GSF-T 136.

[2] Zehlike, L. (2013) Durchführung von Sorptions- und Desorptionsversuchen von Uran(VI) an Montmorillonit, Bachelor thesis, TU Dresden.

Formation of trioctahedral smectite in a 6½ year iron-bentonite large scale field experiment (ABM2) at Äspö hard rock laboratory, Sweden

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In Sweden radioactive waste is to be emplaced in a copper canister with an iron-insert, and the long-term interaction of bentonite and iron or copper is of high interest. In 2006 the ABM experiment started at Äspö Hard Rock Laboratory, Sweden at 450 m depth. Twelve different clay rings (3 dm) were placed onto a heated iron cylinder (~130 ºC). The first package (ABM1) was excavated in 2009 and was analyzed regarding chemistry, mineralogy, hydromechanical properties and microbiology. In 2012 three new experiments were installed (ABM45). In 2013 the second package (ABM2) was excavated, 6½ years after installation.

Here, we have focused on one sample more than the others, a scraping sample from the heater at Febex block 9. This sample was mainly a mixture of magnetite, a trioctahedral smectite and the original smectite. The magnetite was separated with a magnet and the clay was Ca-exchanged. A new XRD reflection at 1.55 Å corresponding to a trioctahedral phase was observed. The intensity relation of the 060 reflections indicated a 35:65 relation between tri to di octahedral smectite. FT IR data using the original smectite and a ferrous reference saponite supported a 40:60 distribution. µ-RAMAN spectra were collected on 20 random ~10x10 µm spots, all had a similar appearance, indicating a very homogenous sample. Some dark particles ~5x5 µm were observed and identified as likely magnetite remainings. Accessory minerals quantified with XRD were subtracted from the chemical content of the sample. The amount of dioctahedral smectite from the 060 intensity relation was subtracted from the original pure smectite. A trioctahedral smectite should ideally have (Mg+Fe)/(Si+Al) = 0.75. The proportion of di:tri smectite was optimized using this ratio, resulting in a 40:60 distribution. The molar content of Mg was somewhat larger than Fe, hence it seems to be saponite. The thermal stability of the phase was investigated and found to be greater compared to the original smectite, which is compatible with saponite.

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

Geochemical modelling of the ABM experiment at Äspö HRL

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Sweden is considering disposal of the High Level Waste in a deep underground repository in granite rock. Bentonite will be used as buffer material surrounding the waste packages and is expected to limit radionuclide migration. Even though MX-80 bentonite is the reference material, different alternatives are being investigated [1]. In 2006, the field experiment Alternative Buffer Materials (ABM) was started at the Äspö Hard Rock Laboratory. Three packages, deposited into 3 m deep boreholes, made of 11 distinct compacted bentonite materials arranged in different configurations have been tested. After installation, packages were saturated and heated to different target values. This work concerns the evolution of Package 1 (initiated in 2006, it ran for ~2.5 years). Examination after retrieval showed significant homogenisation of the initially contrasting cation-exchanger compositions between bentonite blocks [2], recently confirmed in the post-mortem analysis of Package 2. In this work, a modelling study to verify whether this behaviour could be explained by diffusion of major ions and cation-exchange has been undertaken.

The 2D axisymmetric model, implemented in the software Comsol Multiphyics®, considers coupled diffusion and cation-exchange in a stack of 30 bentonite blocks. Effective diffusivities for each block were estimated based on the dry density of the bentonite and temperature evolution.

The model results indicate that the effect of diffusion on homogenisation is significant and can explain quantitatively the observed patterns in the package. The behaviour of major anions is being further investigated to determine whether anion exclusion has occurred to a significant extent. Estimations for different blocks will be presented and compared to experiments. It is shown that the relatively simple model is able to quantitatively describe the main processes leading to homogenisation of the exchanger composition of the different blocks.

Svensson D. et al., 2011. Alternative Buffer Material - Status of the ongoing laboratory investigation of reference materials and test package 1. SKB TR-11-06.

Dohrmann R. et al., 2013. Mineralogical investigations of the first package of the alternative buffer material test II. Exchangeable cation population rearrangement, Clay Minerals, 48, 215-233.

Kinetic experiments and XPS study of uranyl adsorption onto Ca-montmorillonite in the presence and absence of carbonates

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Kinetic experiments of the uranyl (UO_2^{2+}) adsorption onto Ca-montmorillonite in the presence (MC) and absence (MO) of carbonate, and a composite material (kaolinite, montmorillonite and humic acid) were performed using a continuous flow-through reactor. The experiments were carried out at pH 4 using uranyl acetate [$1.0x10^{-4}$M] and sodium acetate [$1.0x10^{-4}$M] to control the ionic strength.

Two different breakthrough (BTC) curves were obtained for each experiment, which corresponds to the adsorption - desorption processes. Both were separated by an equilibrium period, where the steady-state saturation of montmorillonite occurred. To achieve the amounts of UO_2^{2+} adsorbed or desorbed, the area between the theoretical BTC and each experimental BTC was calculated. Higher adsorption capacity after 42 hours was found for MC [adsorbed 12.84 mg (UO_2^{2+})/g], which adsorbed more 25% than MO and more 10% than the composite material. The MC desorbed (1.64 mg (UO_2^{2+})/g) was 66% lesser than MO and 59% than the composite material. The presence of carbonate promoted the adsorption and retention of UO_2^{2+} onto the clay surface.

The best fit to our experimental kinetic data is assigned by intra-particle diffusion model, which shows that uranyl diffusion from the aqueous solution onto montmorillonite surface plays an important role in the adsorption rate.

The XPS spectra corresponding to the $U4f_{7/2}$ core level signals show different binding energies at 381.7 ± 0.3 eV (MC) and 381.1 ± 0.3 eV (MO). A single $U4f_{7/2}$ binding energy located at 381.7 ± 0.3 eV arises from the interaction between free UO_2^{2+} ion and aluminol sheet. The $U4f_{7/2}$ binding energy found at 381.1 ± 0.3 eV is assigned to UO_3 confirming that the U(VI) remained in the same oxidation state upon adsorption.

Laboratory and in-situ testing of gas permeability and self-healing ability of Czech Ca-Mg bentonite

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Bentonite is widely used within construction industry and elsewhere. Due to its very low permeability and high swelling ability the bentonite is used as a sealing barrier in waste sites. Its usage is also envisaged in a deep radioactive waste repository. The waste or the package materials will generate gases within and after the lifetime of these structures; therefore the knowledge of gas migration through the sealing system is essential. The aim of presented research is to experimentally study properties of a Czech Ca-Mg bentonite and thus its suitability for use in construction. Therefore several forms are tested: powder, granules, pellets and their mixtures, or compacted prefabricates. Both in-situ and laboratory experiments are being conducted. All types of these experiments are focused on investigation of bentonite permeability and self-healing ability which are key properties for sealing barriers.

The in-situ experiment, situated at the Josef Underground Laboratory, consists of an instrumented horizontal borehole filled by prefabricated bentonite blocks with a perforated steel tube leading through which serves for water or gas injection. Gas injection tests are dedicated to study changes in permeability when increasing saturation of the bentonite filling. The compacted bentonite is also tested in the laboratory on small-scale cylindrical samples in special cells for the determination of hydraulic and gas conductivity. Large-scale laboratory experiments are dedicated to test bulk bentonite material. The bentonite is compacted or directly sprayed into a steel cell adapted for material saturation and for implementation of gas injection tests. After each test the cell is dismantled and the spatial distribution of dry density and material homogenization is checked.

The results of the testing programme consisting of repeated phases of saturation and gas injection tests for all the experiments show a good self-healing behaviour of the tested bentonite. The variety of performed tests enables to study the effects of different material preparation on the investigated properties and to compare different material forms.

Experimental investigations of piping phenomena by saline water in bentonite based buffer materials for HLW repository

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During the installation of buffer in a deposition hole of HLW repository, water flow may cause piping and erosion of buffer according to its inflow rate, and they may trigger mass redistribution of buffer, sedimentation and material separation of bentonite materials. The authors have conducted piping experiment using distilled water in small scalecontainer with a diameter 100 mm and a height of 50 mm [1]. This paper describes the condition of parameters which cause piping and erosion in case of saline water and the formation of piping, allowable limit of inflow rate in case of Na type bentoniteblock of 70 wt% of Kunigel V1 and 30 wt% of silica sand, or pellet of 100 wt% of Kunigel V1.

This research and development was financed by “Development of Advanced Engineering of the Disposal System, FY2012 and FY2013” from the Agency of Natural Resources and Energy, the Ministry of Economy, Trade and Industry of Japan.

1. K. Suzuki, H. Asano, R. Yahagi, I. Kobayashi, P. Sellin, C. Svemar and M. Holmqvist, Experimental investigations of piping phenomena in bentonite-based buffer materials for an HLW repository, pp363-pp382, Clay Minerals, Vol.48, Number 2, May 2013.

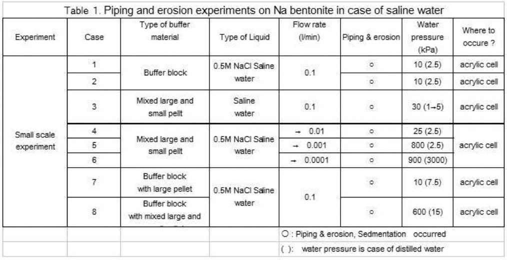

Table 1. Piping and erosion experiments on Na bentonite in case of saline water

Experiment	Case	Type of buffer material	Type of Liquid	Flow rate (l/min)	Piping & erosion	Water pressure (kPa)	Where to occure ?
Small scale experiment	1	Buffer block	0.5M NaCl Saline water	0.1	○	10 (2.5)	acrylic cell
	2				○	10 (2.5)	acrylic cell
	3	Mixed large and small pellt	Saline water	0.1	○	30 (1→5)	acrylic cell
	4	Mixed large and small pellt	0.5M NaCl Saline water	→ 0.01	○	25 (2.5)	acrylic cell
	5			→ 0.001	○	800 (2.5)	
	6			→ 0.0001	○	900 (3000)	
	7	Buffer block with large pellet	0.5M NaCl Saline water	0.1	○	10 (7.5)	acrylic cell
	8	Buffer block with mixed large and			○	600 (15)	acrylic cell

○ : Piping & erosion, Sedmentation occurred

( ): water pressure is case of distilled water

Figure 1. Piping and erosion experiments on Na bentonite in case of saline water

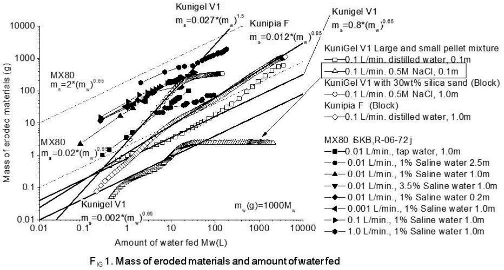

Figure 2. Mass of eroded materials and amount of accumulated water flow

Alteration of nanocrystalline calcium silicate hydrate (C-S-H) at pH 9.2 and room temperature

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In the French design of deep underground radioactive waste disposal, cementitious materials will be used to build access structures, galleries, vaults and waste packages for Intermediate Level Long-lived Waste (ILLW). Part of these cementitious materials will be in physical contact with the Callovian-Oxfordian clay host rock formation (COx). The pH of the COx pore water is around 7 and its composition is very different from the cementitious pore water. Due to this chemical contrast, a chemical gradient will develop at the cement/clay interfaces and will induce mineralogical transformations.

Nanocrystalline calcium silicate hydrates (C-S-H) are the main constituents of concretes and are essential for cohesion of cement paste. It is therefore fundamentally important that we be able to reliably estimate C-S-H weathering/dissolution rates if we wish to estimate the durability of various cementitious materials. In order to mimic a clay/concrete interface, C-S-H alteration was studied with flow-through experiments at 25 °C and pH 9.2. Three materials with apparent Ca/Si ratios of 1.47, 1.38 and 0.86 were investigated. Physical (TGA/DTA), mineralogical (XRD) and chemical (EPMA, TEM/EDX) analyses were performed to characterize the reacting minerals. Initial stoichiometric Ca/Si ratios (C/S) were 1.22, 1.22 and 0.85, respectively. The excess of calcium is attributed mainly to the presence of CH intimately mixed in with C-S-H particles. Under our experimental conditions the stoichiometric C/S ratios decreased continuously with time. C-S-H compositions were monitored during flow-through experiments in order to know the mineral stoichiometry. The kinetics were found to be a function of the C/S. A decrease in layer-to-layer distance in the early stage of the alteration process is interpreted as interlayer Ca/Na exchange. A second dissolution step, marked by the stoichiometric release of calcium and silicate, certainly results from layer dissolution.

Correlation between mechanical properties of the bentonite and its swelling behavior

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Engineered barrier systems (EBS) used in radioactive waste disposal facilities are part of the system which must prevent radionuclide from reaching the biosphere, for up to 1 000 000 years, migrating from deep (more than 300 m), stable geological environment. EBS is the second 'line of defense' against the migration of radionuclides, after the corrosion of containers. They also shield containers from possible environmental impact and the host rock from the heat released by the high level radioactive waste (HLW) and/or spent nuclear fuel (SF). Engineered barrier systems are usually made of cement, salt, clay (bentonite) or clay/rock mixtures.

Quality control tests of clays are the same for all engineered barrier systems either used in the environmental engineering or standard geotechnical constructions. Differences may show up in the special required criteria related to specific application. Recommended clay properties depend also on the type of host rocks. Standard quality control procedures for bentonite used as a sealing barrier in radioactive waste disposal sites are described as some personal experiences.

The research to determine correlation between mechanical properties of the bentonite and its swelling behavior was conducted on the granular bentonite. X-ray powder diffraction showed that the bentonitne contains 80-85% of montmorillonite. Bentonite properties were as follows: liquid limit 437%, plastic limit 53%, specific surface area 700 m^2/g and CEC 89 meq/100 g. The influence of swelling on the bentonitne shear strength was studied in the direct shear device. During this process, hydration times (7 to 21 days) were changed in a series of tests at different normal stresses (50 to 200 kPa) simulating bentonite clay swelling. The impact of swelling on the bentonitne consolidation and hydraulic properties were studied in oedometer device and triaxial device under isotropic compression conditions. Demineralized water was used as the test fluid.

Primary swelling phase was reached after 31 days regardless of the intensity of the normal stress. Shear tests show a significant reduction in cohesion with the extension of the hydration of bentonite, and the friction angle increases with hydration. There is no significant change in the value of the friction angle by extending hydration after 14 days.

Effects of chemical structure on stability of smectites in short-term alteration experiments

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Because of their isolating capacity smectite-rich clays have been proposed for use as buffer and backfill materials in high-level radioactive waste (HLW) repositories. Short-term alteration process of smectites in twenty five different clays and bentonites were investigated. These were saturated for 30 days in NaCl-solution and deionized water then were overhead-shaken with speeds of 20 and 60 revolutions per minute (rpm). The initial materials and reaction products were investigated by transmission electron microscope with energy-dispersive X-ray (TEM-EDX), X-ray diffraction (XRD), X-ray fluorescence (XRF), and Fourier Transform Infrared Spectrometry (FT-IR).Depending on composition of the octahedral and interlayer sheets, each of the smectites studied showed its potential of dissolution. The higher the content of octahedral Fe and Mg compared to octahedral Al, the higher the specific dissolution potential. The bentonites were classed as “Sleeper”, “Intermediator”, or “Sprinter” corresponding to a relatively low, medium, or high specific dissolution potential, respectively. In addition, in experiments with 20 rpm (low energy level) these bentonites could be classified into two types based on the cation in the octahedral sheet of the initial smectite: (i) type A: $Al_{VI} > 1.4$ and $Fe_{VI} > 0.2$ (per $[O_{10}(OH)_2]$), (ii) type B: $Al_{VI} > 1.4$ and $Fe_{VI} < 0.2$ or $Al_{VI} < 1.4$ and $Fe_{VI} > 0.2$ (per $[O_{10}(OH)_2]$). The smectites could be ordered into type A or B by interpretation of the TEM-EDX and FT-IR data. The cation composition and position in the lattice plane of the interlayer sheet affected the specific dissolution potential of smectites. Smectites of type A with Na as the stabilizing interlayer cation, and smectites of type B with stabilization of quasicrystals by Ca and Mg both acted as “Sleepers”. In experiments with 60 rpm (high energy level), all smectites have shown only the behavior of type A with Na as stabilizing cation in interlayer sheets

Bentonite pellets for use as gap filling

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For safe radioactive waste disposal must be done a number of the requirements. The basic requirement is to ensure the isolation of extremely dangerous radionuclides for a long time. Research on engineered barriers designed to isolate radionuclides takes place in the world for decades. Vertical disposal system of spent nuclear fuel is well developed in general scope, but some problems still exits. The construction of the disposal hole will exert an influence on the geotechnical properties of the buffer material. According to the vertical disposal system the disposal well will be drilled into the rock massif with a diameter which will allow for the installation of bentonite blocks around the container. The disposal well will be drilled into the bedrock with a diameter which allowed for the subsequent installation of both the bentonite blocks (buffer) and the container itself. Inevitably gaps will remain following container installation: the first gap is that between the container and the bentonite blocks (container-buffer gap) and the second is that between the bentonite blocks and the rock massif (rock-buffer gap). The objective of this work was to improve the properties of the backfill in the latter gap, i.e. that between the rock massif and the buffer. The dimensions of and the backfill employed in the gap could have a significant influence on the sealing material and its properties. The objective of this study therefore was to investigate both the methods and materials which might be used for the filling of the gap between the rock wall of the disposal well and the bentonite blocks. The results from the small scale tests show dry density on the level needed by buffer design properties.

Preparation of Slovak HDTMA-bentonite for U(VI) adsorption study

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The natural sorbents- bentonites applied to the adsorption of uranium offer many advantages (availability, high sorption capacity, good hydraulic properties etc.) as well as no introduction of additional pollution to the environment in the case of application as permeable reactive barriers. Slovak bentonite deposits Jelšový potok and Kopernica have great potential for use as a engineering barriers in multibarrier systems of radioactive waste repositories as well as deep geological repository for high level radioactive waste and spent nuclear fuel. In our work, HDTMA-modified bentonites were prepared and their sorption properties towards cationic and anionic uranium species were investigated. The removal of uranium species from aqueous solutions (initial concentration: 10 - 1,000 mg/L) was determined spectrophotometrically using the Arsenazo III method. The sorption behavior was studied by batch technique. The maximum removal for uranium cationic species was observed from solutions of initial $pH_{init} = 2.5$ whereas for anionic species of $pH_{init} = 8.5$. The experimental data reproduced very well by the Langmuir equation. The U(VI) sorption kinetics were fitted using the pseudo-first and the pseudo-second order equations at three different temperatures (T = 298; 308; 318 K).

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Na-montmorillonite microstructure

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MX-80 bentonite is a reference material for the clay planned to form a part of a deep geological disposal of high-level nuclear waste in several countries. In this study homoionic sodium montmorillonite obtained from purification of the MX-80 clay is used as a simplified system to study its microstructure. The research involved a set of complimentary methods: small angle X-ray diffraction, nuclear magnetic resonance, transmission electron microscopy and ion exclusion. Investigated samples were compacted and water saturated at the dry density in the range of 0.5 - 1.5 g/cm^3. Different methods provide similar quantification of the water present in the interlamellar pores, therefore giving support to the multiple porosity concept of bentonite microstructure.

Bentonite erosion and colloid mediated transport of radionuclides in advection controlled systems

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The multi-barrier system of a nuclear waste repository consists basically of the technical, the geotechnical and the geological barrier. The backfill material forms the geotechnical barrier and surrounds the canister. Compacted bentonite is considered to be suitable for this purpose due to its swelling properties that control the transport of water by diffusion and its high sorption capacity effectively retaining of radiotoxic elements.

In the case of canister corrosion, radionuclides can get in contact with the compacted bentonite and sorption on the bentonite surface will take place under pore water conditions (Fernandez et al.). During future glaciation dilute melt water may intrude down to repository depths and come in contact with the compacted bentonite. Thereby, gel layer formation in the contact zone and successive bentonite erosion might occur and colloid associated radionuclides might be released to the repository far-field.

Different bentonites (Febex, MX-80 and Calcigel) are used for colloid generation. They are generated in static batch and transient erosion experiments under advective flow conditions and characterized concerning (i) colloid size and mass via Laser Induced Breakdown Detection (LIBD), s-Curve-LIBD (Delos et al., 2008), and AFM and (ii) mineralogy via ICP-OES, ICP-MS and SEM-EDX.

Radionuclide sorption and desorption experiments on bentonite colloids are carried out under bentonite pore water conditions followed by desorption experiments under natural granitic Grimsel ground water conditions. The desorption is investigated both by static batch and flow-through experiments. Radionuclide cocktails are used containing Curium for time resolved laser fluorescence spectroscopy (TRLFS) and other radionuclides in accordance to the Colloid Formation and Migration (CFM) project at the Grimsel Test Site (Switzerland).

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In-situ study of bentonite interaction at temperature up to 95 °C

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Bentonite clays are considered to be one of the most suitable natural sealing materials. For example, they are used to prevent water to reach materials which need a long-term protection, or to prevent pollutant leaks into the environment. Safety precautions are required for underground openings containing heat-producing sources (e.g. energy storage and heat-producing waste disposal).

Applied research on thermohydromechanical and chemical (THMC) coupling on granite-bentonite-metal boundaries is in progress in the research gallery Mokrsko - Underground Laboratory Josef (Czech Republic). A special bentonite container has been introduced into a water saturated granite environment. Subsequently, the container has been heated up to up to 95 °C. The experiment, which is running for 2 years at the moment, is scheduled to conclude in 2015.

Natural Ca-Mg bentonite from Černý vrch (CZ) has been selected for the experiment. The container, a bentonite cylinder 700 mm in diameter and 2210 mm long made of compressed bentonite blocks, embodies a heat source. In addition, various metal material samples have been placed inside the container at two levels. During the experiment, the swelling pressure, temperature and electrical properties inside the body are being monitored and evaluated. In five surrounding wells, hydrogeology and hydrochemistry of groundwater is monitored. Furthermore, geoelectrics and GPR are being carried out on regular basis.

Various laboratory tests were employed to quantify important characteristics of the selected bentonite including the hydraulic conductivity, swelling pressure, plasticity index, uniaxial compressive strength and thermal conductivity. Geochemistry of the bentonite and rock environment is studied in detail. After termination of the experiment, a comparative geochemical analysis and geotechnical tests is scheduled.

To mitigate risk of experiment bias during bentonite sampling three additional smaller (76 mm in diameter) physical models were built. These models provided insight into the THMC changes both in the bentonite and on the bentonite-granite boundary after 6 and 12 months. The models were sampled by overcoring periodically.

The research was supported by the Ministry of Industry and Trade of the Czech Republic under project FR-TI4/497.

Monte Carlo and Molecular Dynamic simulations addressing the tactoid formation and swelling of charged clay platelets

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The free energy of interaction between parallel charged platelets has been calculated using Monte Carlo simulations. The platelets are primarily intended to represent clay particles. With divalent counterions, the free energy for two platelets or two tactoids (clusters of parallel platelets) shows a minimum at a short separation due to the attraction caused by ion correlations. In a salt-free system, the free energy of interaction has a long-range repulsive tail beyond the minimum. The repulsion increases for tactoids with larger aggregation numbers, while the depth of the free-energy minimum is gradually reduced. For large enough aggregation numbers, the repulsion is dominating and the minimum is no longer a global free-energy minimum. This is an effect of a depletion of counterions free in solution (outside tactoids) as counterions and platelets aggregate into tactoids and the resulting redistribution of counterions in the system changes the effective interactions between platelets and tactoids. The difference in tactoid-tactoid interactions as a function of aggregation number can be removed by adding enough salt to mask the depletion. Adding salt also reduces the repulsive tail of the free energy of interaction and enhances the minimum. No dependence on the aggregation number suggests that an isodesmic model with a monotonically decaying distribution of aggregation numbers can be used to describe a clay system. This may help explain the experimental observations of low average numbers of platelets in tactoids, although factors not included in the simulation model may also play an important role. The effect seen in the salt-free case opposes the formation of tactoids and would reduce the average aggregation number further.

Alteration of clay minerals under the influence of acid solutions that accompany radioactive wastes

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A possible way of low and middle active radioactive wastes disposal is liquefaction and injection to the deep layers-reservoirs, constrained between confining clay layers. Such wastes consist primarily of acid and alkaline solutions. In the majority of cases calculation of clay barrier stability or pollutant migration analysis is based on constant properties of migration media. Although many researches show that clays structure and properties may change profoundly after an acid and alkaline treatment. It changes dynamics of wastes migration through reservoir rocks and confining layers. The present work is aimed to reveal possible transformations of clay minerals under an acid treatment for further use in a waste migration analysis.

First of all sandstones from the reservoir layers were studied. Samples were collected inside and outside the influence zone of wastes.

Detailed study of the clay fraction allowed us to distinguish authigenic minerals that were formed as a result of catagenesis from those that were formed as a result of technogenic processes.

Obtained results allow us to suggest that isolation property of geological environment in the waste site remains sustainable. Feldspar and dark-colored minerals‘ leaching may cause an increase of permeability, however new formations of smectite aggregates in big pores most probably will neutralize this effect.

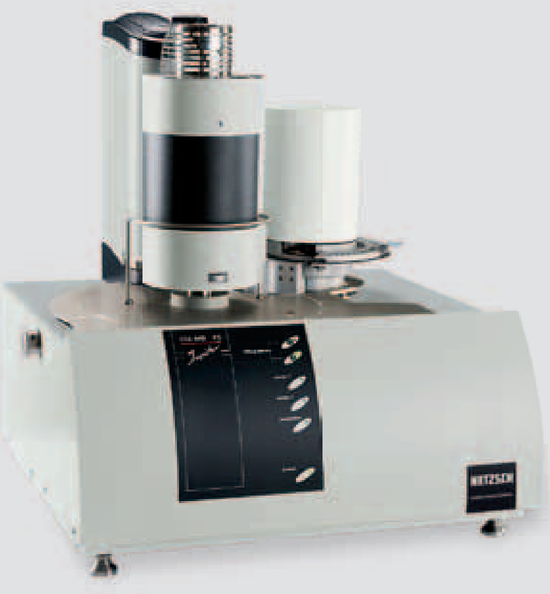
To confirm a possibility of clay minerals‘ transformation in a way that was observed in samples from the disposal site we carried out laboratory experiments. Kaolinites, chlorite and smectite were used as objects because they are predominant components of clay fraction in reservoir layers. These minerals were treated with 1M HNO_3 solution at 60 °C with different duration.

In a result of treatment octahedral sheets were destructed. The degree of destruction was the more the longer the treatment time was. Tetrahedral sheet disintegrated and tended to amorphous state. It has been seen on TEM micrographs and proven with XRD by gradual disappearing of 00l reflection series and with FTIR spectroscopy by disappearing of Al-Al-OH band and also shifting of Si-O band to wavenumber that corresponds to amorphous Si-O bonding.

Index of Authors

Index of Authors

Index of Authors

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