

3rd Mid-European Clay Conference – MECC 06
Abstracts Book

edited by Igor VLAHOVIĆ, Darko TIBLJAŠ, Goran DURN & Vanja BIŠEVAC

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CONTENTS

KEYNOTE ABSTRACTS

BAHRANOWSKI, K. & SERWICKA, M.: Layered minerals in catalysis.....	3
CUADROS, J.: Clay minerals in the making.....	4
DOHRMANN, R., RÜPING, K., KLEBER, M. & JAHN, R.: XRD texture measurements of oriented clay aggregates – a quantification tool.....	5
MADEJOVÁ, J.: Near infrared spectroscopy: a powerful method to learn more on modified smectites.....	6
MURAD, E.: Mössbauer spectroscopy of geological materials.....	7
PETIT, S., JOUSSEIN, E. & GRAUBY, O.: New insight into halloysite physico-chemical properties.....	8
RAUCSIK, B., RAUCSIK-VARGA, A., SZAKMÁNY, Gy. & KOVÁCS-KISS, V.: Clay mineralogy, petrography and geochemistry of Late Palaeozoic siliciclastic rocks from the Mecsek–Villány area (SW Hungary): implications for source-area weathering, provenance and diagenesis.....	9
RUIZ-HITZKY, E.: Clay-based bionanocomposites.....	10
TIBLJAŠ, D. & ŠČAVNIČAR, S.: Zeolite deposits in Croatia.....	11
ZNIDARČIĆ, D.: Engineering properties of clays.....	12

ABSTRACTS

ABU-JDAYIL, B. & AL-MALAH, K.: Waterproof polymeric heat insulators based on clay fillers: mechanical properties.....	15
ACTIŃŠ, A., SUPE, L. & SARCEVIČA, I.: Latvian smectite clay and bentonite interaction with tetraoctyl-ammonium bromide.....	16
ADAMCOVA, R., HAASOVA, Z. & MAAS, P.: Engineering geological research of highly compacted bentonites in Slovakia.....	17
AL-JUBOURY, A.: Clay mineralogy in northern Iraq during the Miocene: paleoenvironmental indicators.....	18
ANDREJKOVIČOVÁ, S., JANOTKA, I. & KOMADEL, P.: Phase composition and geotechnical evaluation of bentonite from Lieskovec, Slovakia.....	19
ARANDA, P., MANOVA, E., MARTÍN-LUENGO, M.A., LETAĀEF, S. & RUIZ-HITZKY, E.: TiO ₂ /delaminated-clay nanocomposites.....	20
AUGUST, C.: Mineralogy of a Carboniferous bentonite from the Sudetes (SW Poland), northern margin of the Bohemian Massif – preliminary data.....	21
BALOGH, K., ÁRKAI, P., JUDIK, K., ITAYA, T., HYODO, H. & BALOGH, I.: Development of a simple method for Ar/Ar dating of micrometer-sized minerals: a progress report.....	22
BARUDŽIJA, U., TADEJ, N. & TADEJ, J.: Clay minerals assemblage in the Upper Albian carbonate succession (Tinjanska Draga, Istria, Croatia).....	23
BAYHAN, E.: Upper Cretaceous–Lower Tertiary clay mineral successions of southern Haymana region (Ankara, Turkey).....	24
BAYHAN, H., GÜLEÇ, F., BAYHAN, E., TEMEL, E. & HÜRYILMAZ, H.: Clay mineralogy of Tertiary sedimentary sequence from Gökçeada Island (northeast Aegean Sea, Turkey).....	25
BIŠEVAC, V., BALEN, D., BALOGH, K. & TIBLJAŠ, D.: K–Ar dating of Cretaceous metamorphism recorded in the eastern part of Mt. Papuk, Slavonia, Croatia.....	26
BISHOP, J.L., BROWN, A.J., CLOUTIS, E., DYAR, M.D., HIROI, T., LANE, M.D., MILLIKEN, R.E., MURAD, E. & MUSTARD, J.F.: A multispectral study of clay minerals: Mössbauer, reflectance, transmittance, and emission spectroscopy.....	27
BLANCO GARCÍA, I., LUQUE, J., BARRENECHEA, J.F., AZCARATE, J.A., ELSESEN, J., RODAS, M., SWENNEN, R., SÁNCHEZ, C.J. & DONDI, M.: Production of synthetic lightweight aggregates (LWA) from mining wastes.....	28
BLANCO GARCÍA, I., SWENNEN, R. & ELSESEN, J.: Physical properties and behaviour during leaching of synthetic aggregates made with polluted dredged sediments from Flanders, Belgium.....	29

BOJAR, A.-V., OTTNER, F., GRIGORESCU, D. & CSIKI, Z.: Maastrichtian calcisols from the Hateg basin, South Carpathians: mineralogical and stable isotopic investigations.....	30
BRUS, J., URBANOVA, M., KOLOUSEK, D. & ANDERTOVA, J.: Solid-state NMR study of stability of “geopolymers” prepared from alkaline activated metakaoline.....	31
BUJDÁK, J., IYI, N. & CZÍMEROVÁ, A.: Clay mineral template-controlled formation of molecular assemblies of rhodamine 6G.....	32
ČEKLOVSKÝ, A. & BUJDÁK, J.: Spectroscopic study of interaction of porphyrin dyes with layered silicates.....	33
CERJAN-STEFANOVIĆ, Š., ZABUKOVEC-LOGAR, N., MARGETA, K., ŠILJEG, M. & VOJNOVIĆ, B.: Metal complex exchange in natural zeolites.....	34
CZÍMEROVÁ, A., BUJDÁK, J. & IYI, N.: Energy transfer between cations of laser dyes in dispersions of reduced charge montmorillonites.....	35
DAINYAK, L.G.: A new approach to the interpretation of Fe ²⁺ quadrupole doublets in Mössbauer spectra of dioctahedral <i>trans</i> -vacant micaceous minerals.....	36
DELLISANTI, F., MINGUZZI, V. & VALDRÈ, G.: Influence of controlled mechanical deformation on structural, thermal and technological properties of commercial talc.....	37
DILL, H.G., SACHSENHOFER, R., GRECULA, P., SASVÁRI, T., PALINKAŠ, L.A., BOROJEVIĆ ŠOŠTARIĆ, S., STRMIĆ PALINKAŠ, S., PROCHASKA, W., GARUTI, G., ZACCARINI, F., ARBOUILLE, D. & SCHULZ, M.: The origin of mineral and energy resources of Central Europe (accompanied by metallogenic map 1:2.500,000).....	38
DOBNIKAR, M., DONDI, M., MIRTIC, B., ROKAVEC, D. & ZANELLI, C.: Mineralogical transformations during firing of some Plio–Quaternary clays from NE Slovenia.....	39
DOMINKOVIĆ ALAVANJA, S. & OREŠKOVIĆ, J.: Application of IP method for discovering clay zones in carbonate terrains.....	40
DOUŠOVÁ, B., GRYGAR, T., MARTAUS, A., KOLOUŠEK, D., FUITOVÁ, L. & MACHOVIČ, V.: Mechanism of As sorption on Fe-treated clays.....	41
DURN, G., MINDSZENTY, A. & GERMAN-HEINS, J.: Micromorphology of the pedo-sedimentary colluvial complex in Sjenokoša (Istria, Croatia).....	42
DURN, G. & OTTNER, F.: Clay minerals in Jurassic bauxites and associated cover “blue hole” sequence (Istria, Croatia).....	43
DYAR, M.D., BISHOP, J.L. & DRIEF, A.: The influence of physical alteration on the Mössbauer and reflectance spectra of antigorite and applications to soil alteration processes on Mars.....	44
FLECK, G., PUDEL, F., MÖRL, L., RANGELOWA, J. & KRÜGER, G.: Fluidised bed technology for drying and milling of clay minerals.....	45
GALOVIĆ, L., MILEUSNIĆ, M., PEH, Z., DURN, G. & HALAMIĆ, J.: Mineralogical and geochemical characteristics of loess/paleosol section in Šarengrad, Srijem, Croatia.....	46
GAUTIER, M., MULLER, F., ALBÉRIC, P., LE FORESTIER, L., BÉNY, J.-M. & BAILLIF, P.: Behaviour of carboxylic acids on NH ₄ -smectites: pollution prediction in waste landfill.....	47
GERARDI, J.: Barrier characteristics of clay and claystone: the BETTON database.....	48
GOMES, C.S.F.: 1773: The year of the first manufacture of porcelain in Portugal.....	49
GOMES, C.S.F. & PERTEIRA SILVA, J.B.: Clay-based formulations to be used in topical applications.....	50
GOREA, M., BENEA, M. & MARIŞ, C.: Physico–chemical and mineralogical characterization of the Hălmagiu clay (Arad county, Romania), a raw material for ceramic industry.....	51
GÓRNIK, K.: The structure and diagenetic transformation of illite/smectite from marls of the Polish Flysch Carpathians.....	52
GÓRNIK, K., BAHRANOWSKI, K., GAWEL, A., RATAJCZAK, T. & SZYDLAK, T.: Thermal properties of illitic material from Lower Carboniferous black shales (Western Pomerania, N Poland).....	53
GREGOR, M., HARMADYOVÁ, K. & ČAMBAL, R.: Mineralogical and petrographical analysis of Kalenderberg household ceramic from Devín Castle (Slovakia).....	54
HONTY, M., ŠUCHA, V., KOMADEL, P., OSACKÝ, M., MADEJOVÁ, J., VALÚCHOVÁ, J., BUJDÁK, J. & UHLÍK, P.: Experimental study of iron–bentonite and pyrite–claystone interaction at low temperature.....	55
HRACHOVÁ, J., CHODÁK, I. & KOMADEL, P.: Vulcanized rubber filled with modified montmorillonite.....	56

HRUSKOVA, M., GRYGAR, T. & HRADIL, D.: Fast determination of CEC by Cu-trien method, its limitation and use.....	57
IONESCU, C., GHERGARI, L., HOECK, V., SIMON, V. & HORGA, M.: Thermal alteration of mineral phases in Bronze Age ceramics from Transylvania (Romania).....	58
JANOTKA, I. & GALKO, I.: Cement suspensions for slurry cut-off walls with ultra fine ground Na-bentonite from Lieskovec and Jelšovský potok deposits.....	59
JUDIK, K., RANTITSCH, G., RAINER, T.M., TIBLJAŠ, D. & ÁRKAI, P.: Correlation of organic and inorganic temperature indicators – a case study on low-temperature metamorphic rock series from Mt. Medvednica, Croatia.....	60
KAPUSTIN, A.E., KOZLOVSKIY, R.A. & BISH, D.L.: The structure and chemistry of natural takovite and synthetic analogue of takovite.....	61
KAUFHOLD, S. & DOHRMANN, R.: Detachment of colloids from bentonites in water.....	62
KELE, S., DE CRAEN, M., VAN GEET, M. & LIAN, W.: Geochemical studies on pore water from two different clay types in the frame of radioactive waste disposal researches.....	63
KHANKHASAEVA, S.Ts., BADMAEVA, S.V., DASHINAMZHILOVA, E.Ts. & DOBOLOVA, U.V.: The synthesis of iron-containing pillared clays from natural clays of Transbaikalia and research of their catalytic properties in wet oxidation of phenol by hydrogen peroxide.....	64
KŁAPYTA, Z.: Structural heterogeneity of alkylammonium-exchanged synthetic swelling fluoromicas.....	65
KLIKA, Z., ČAPKOVÁ, P., HORÁKOVÁ, P., VALÁŠKOVÁ, M. & POSPÍŠIL, M.: Intercalated montmorillonites by different aggregates of methylene blue.....	66
KNIEWALD, G. & FIKET, Ž.: Sorption of arsenic on clay minerals – a theoretical approach.....	67
KOLOUŠEK, D., VOREL, J., DOUŠOVÁ, B., URBANOVÁ, M., BRUS, J., SLAVÍK, R., ANDERTOVÁ, J., MACHOVIČ, V., BÍLEK, V. & HÁJEK, P.: Hydrothermal stability of geopolymers.....	68
KOMADEL, P. & STUCKI, J.W.: Iron phases occurring in Fe-rich bentonite from Lieskovec, Slovakia.....	69
KOVAČEVIĆ ZELIĆ, B., DOMITROVIĆ, D., MILEUSNIĆ, M. & TADEJ, N.: Chemical compatibility of GCL mineral component to site-specific liquid.....	70
KOVÁCS, J.: Geochemistry and weathering of the Late Cenozoic red clays in the Pannonian Basin.....	71
KOVANDA, F., ROJKA, T., MACHOVIČ, V. & BEZDIČKA, P.: Thermal behaviour of synthetic takovite-like anionic clays studied by high-temperature X-ray diffraction and Raman spectroscopy.....	72
KRUPSKAYA, V., VOEVODIN, L., PILOYAN, G. & NIKOLSKIJ, M.: Smectites from Ziryanovskoe deposit (Kurgan Region, Russia): Relation between composition, structure and technological properties.....	73
KUSHCHEVA, Y.V., GOLOVIN, D.I. & BUJAKAITE, M.I.: The possibility of the isotopic dating stages of postsedimentary transformations of clayey terrigenous deposits in the different geodynamical situations.....	74
LE FORESTIER, L., BAILLIF, P., PROUST, C. & MULLER, F.: Evolution of swelling and hydration properties of a compacted hectorite percolated by nickel solutions.....	75
LERF, A., WAGNER, F.E., POYATO, J., RAMÍREZ-VALLE, V. & PÉREZ-RODRÍGUEZ, J.L.: Fe ³⁺ intercalation into vermiculite or deposition of iron oxyhydroxides? A Mössbauer spectroscopic investigation.....	76
LIEBER, D. & STANJEK, H.: Point of zero charge and surface acidity constants of Fe(OH) ₂	77
LUGOVIĆ, B., CRNJAKOVIĆ, M. & BIŠEVAC, V.: Mineralogical signatures of weathered Late Holocene ash layer from the island Mljet in Croatia.....	78
MAJDÁN, M., KRAUS, I. & GALKO, I.: Geological prospecting of kaolin and kaolinite clays deposits on territory of the Western Carpathians (Slovakia).....	79
MAQUEDA, C., SANTASROMERO, A., MORILLO, E., PÉREZ-RODRÍGUEZ, J.L., LERF, A. & WAGNER, F.E.: Mössbauer spectroscopy investigation of ground and acid treated vermicullite.....	80
MILDER, O.B., PIKULEV, A.I., SEMIONKIN, V.A. & NOVIKOV, E.G.: Particularities of Mössbauer spectroscopy for the archaeological potsherds dating.....	81
MOCKOVČIAKOVÁ, A. & ŠTYRIAKOVÁ, I.: Characterization of changes of low and high ordered kaolinite after bioleaching.....	82
MULLER, F., BÉNY, J.M. & GAUTIER, M.: Intercalation of aniline in Wyoming montmorillonite exchanged with different cations.....	83

MÜLLER, R., VALÚCHOVÁ, J., CALBERG, C., JÉRÔME, R. & GRANDJEAN, J.: Structure and dynamics of cationic surfactants intercalated in synthetic clays.....	84
MUTLU, H., ALTUNEL, E. & UYSAL, I.T.: Dating of fault clays of the North Anatolian Fault Zone, Turkey.....	85
NAGY, N.M. & KÓNYA, J.: Preparation of noble metal bentonites for catalytic purposes.....	86
NÉMETH, T. & SIPOS, P.: Nature and alteration of clay minerals in brown forest soil profiles (Luvisols) of Cserhát Mountains (North Hungary).....	87
OTTNER, F., SIEGHARDT, M., ERSTIĆ, T. & MILEUSNIĆ, M.: Clay minerals and selected ecological aspects of soils on the island Veliki Brijun, Croatia.....	88
PÁLKOVÁ, H., ZIMOWSKA, M., SERWICKA, E.M. & KOOLI, F.: Influence of the synthesis conditions on the physico-chemical characteristics of porous clay heterostructures.....	89
PAPP, H., PERESSON, M., ROETZEL, R. & WIMMER-FREY, I.: Brick kilns of northern Lower Austria: History and geology.....	90
PENTRÁK, M. & MADEJOVÁ, J.: Acid treatment of clay minerals: a FTIR spectroscopic study.....	91
PERIĆ, J., VUKOJEVIĆMEDVIDOVIĆ, N. & TRGO, M.: The equilibrium isotherm for lead removal by natural zeolite-clinoptilolite: a comparison of batch and column methods.....	92
PINTO DE JESUS, A. & ROCHA, F.: Clay mineralogy and crystallochemistry of the Douro Carboniferous Basin (Early Stephanian C; NW Portugal).....	93
PODE, R., POPOVICI, E., COCHECI, L., REISZ, E. & SEFTEL, E.M.: Sorption equilibrium of phosphate anion on Mg _x Zn _{3-x} Al-type hydrotalcites.....	94
POP, D., TÓTH, E., WEISZBURG, T.G., SÁSÁRAN, E. & STICHLEUTNER, S.: The TOT layer silicate of the lacustrine green clay, Rona limestone, Romania.....	95
POPOVICI, E., PODE, R., REISZ, E., COCHECI, L., PODE, V. & SEFTEL, E.M.: Sorption kinetics and equilibrium of thiocyanate anion on Mg _x Zn _{3-x} Al-type hydrotalcites.....	96
POPOVICI, E., VASILE, A., PODE, R., DVININOV, E. & REISZ, E.: Use of Romanian clays for textile wastewater depollution.....	97
POSPÍŠIL, M., VETEŠKA, M., ČAPKOVÁ, P., BENEŠ, L., MELÁNOVÁ, K. & ZÍMA, V.: Structure analysis of hydrotalcite intercalated with pyrenetetrasulphonate acid, molecular simulations and experiment.....	98
PRAUS, P., TURICOVÁ, M., ŠTUDENTOVÁ, S. & KARTOŠOVÁ, G.: Modification of the montmorillonite surface with cationic surfactants.....	99
RAUCSIK, B. & VARGA, A.: Climato-environmental controls on clay mineralogy of the Hettangian-Bajocian successions of the Mecsek Mountains (Tisza Mega-unit, Hungary).....	100
REATTO, A., BRUAND, A., MARTINS, E.S., MULLER, F., SILVA, E.M., GUIMARÃES, E.M. & BROSSARD, M.: Mineralogy of Latosols along a regional toposequence across the Central Plateau (Brazil): First results.....	101
RODRÍGUEZ MARTÍN, J.A., MORALES HERRAIZ, D. & GRAU CORBI, J.M.: Relationship between heavy metals and clay in Spanish agricultural topsoils.....	102
ROJKA, T., KOVANDA, F., DOUŠOVÁ, B. & KOLOUŠEK, D.: Phase transformations of Co-M ^{III} layered double hydroxides (M ^{III} = Al, Cr, Fe, or Mn) during thermal treatment.....	103
ŠEGVIĆ, B., TOŠEVSKI, A., ŠTEVANIĆ D., BIŠEVAC, V. & LUGOVIĆ, B.: Altered tephra layers in the Upper Jurassic Lemeš deposits near Maovice (Dalmatia, Croatia): clay mineralogy and basic soil mechanic properties.....	104
SONDI, I. & VDOVIĆ, N.: Properties of clay mineral surfaces modified by intensive physical disintegration.....	105
ŠRODOŇ, J. & McCARTY, D.K.: Total surface area, surface charge density, cation exchange capacity and water retention in smectites.....	106
STARZEC, K. & SKIBA, M.: Identification of glauconite-smectite interstratification using computer simulations in NEWMOD [®] program.....	107
STRÍČEK, I., UHLÍK, P., ŠUCHA, V., ADAMCOVÁ, R., ČAPLOVIČOVÁ, M. & GALKO, I.: Effect of bentonite compaction on the orientation of smectite particles.....	108
STUCKI, J.W., LEE, K., GOODMAN, B.A. & KOSTKA, J.L.: Effects of <i>in situ</i> biostimulation on iron mineral speciation in a sub-surface soil.....	109
ŠTYRIAK, I., ŠTYRIAKOVÁ, I., ŠPANOVÁ, A. & RITTICH, B.: Bacterial destruction of smectite and bacterial DNA bound in smectite-bearing sediments.....	110

ŠTYRIAKOVÁ, I. & ŠTYRIAK, I.: Bacterial removal of Fe(III) impurities from clay: A potential new technology...	111
SZELIGA, W.: Clay minerals (I/S, kaolinite) in contact metamorphism related to Tertiary basalts intrusions in Lower Silesia (Poland).....	112
TIBLJAŠ, D., AVANIĆ, R. & HANŽEL, D.: Glauconitic materials from Lower Miocene Macelj Formation (NW Croatia) – new data.....	113
TIBLJAŠ, D., BALEN, D., MAHEČIĆ, S., KOVAČIĆ, M., JOZIĆ, D., ŠPANIĆ, D., JUDIK, K. & ÁRKAI, P.: Clay minerals as indicators of thermal history of Palaeozoic rocks from Marija Gorica Hills, NW Croatia.....	114
TOMBÁ CZ, E. & SZEKERES, M.: Comparing surface charge heterogeneity of 1:1 with 2:1 type clay particles in aqueous suspension.....	115
TÓTH, E. & WEISZBURG, T.G.: Two in one: two different glauconite series from the same rock, Sümeg Marl Formation, Lower Cretaceous, Bakony Mountains, Hungary.....	116
UHLÍK, P., ČIHÁK, J., TUČEK, L., MALACHOVSKÝ, P. & DERCO, J.: Mineralogy of glauconite-rich sand deposits in the Southern Slovakia.....	117
VÁGVÖLGYI, V., KRISTÓF, J., HORVÁTH, E. & FROST, R.L.: Surface reactivity investigation of mechanochemically activated kaolinite.....	118
VAN CROMPHAUT, C., DE RESENDE, V.G., DE GRAVE, E., KLINGELHÖFER, G., VAN ALBOOM, A. & VANDENBERGHE, R.E.: Iron oxides on Mars: their characterization from MER Mössbauer spectra.....	119
VAVROVÁ, J., BIROŇ, A., GALKO, I. & MAJDÁN, M.: Mantiennite from Pinciná alginite deposit (Slovakia).....	120
VICZIÁN, I., DEZSŐ, J. & RAUCSIK, B.: Mineralogy of fine-grained sediments related to karst phenomena in Vülány Mts., SE Transdanubia, Hungary.....	121
WEISZBURG, T.G., TÓTH, E. & POP, D.: Continuous crystal chemical space for the dioctahedral iron-rich micas and related phases (celadonite, glauconite, Fe-illite).....	122
WYSZOMIRSKI, P.: Triassic red clays in Poland and their importance for ceramic industry.....	123
ZAGÓRSKI, Z. & GRELA, S.: Preliminary mineralogical characteristics of soils developed from Lower Triassic clay deposits (Buntsandstein) in the Holy Cross Mts. (S Poland).....	124
ZAITSEVA, T.S., GOROKHOV, I.M., IVANOVSKAYA, T.A., MELNIKOV, N.N. & YAKOVLEVA, O.V.: Mineralogy, Mössbauer characteristics and isotope age of Middle Riphean glauconites (the Olenek Uplift, Northern Siberia).....	125
ZIMOWSKA, M., PLONA, J., MICHALIK-ZYM, A. & SERWICKA, E.M.: Influence of the synthesis condition on Cu–Mn layered double hydroxides.....	126
ZVIAGINA, B.B.: Crystal-chemical factors affecting the distribution of octahedral cations over <i>cis</i> - and <i>trans</i> -sites in dioctahedral smectites.....	127

Keynote Abstracts

Layered minerals in catalysis

Krzysztof BAHRANOWSKI¹ and Ewa M. SERWICKA²

Among the layered minerals, which have attracted most of the attention concerning the development of novel catalytic materials, clays, silicates and double hydroxides play the dominant role. Historically documented use of layered minerals as catalysts dates back to 1783, when Joseph Priestley described the reaction of ethanol dehydration to ethylene, prompted by the presence of clay. The advent of industrial application of clay catalysts was associated with the introduction, shortly before the Second World War, of a new technology of crude oil refining, known as catalytic cracking, which used acid activated bentonite as a catalyst. The use of clay catalysts dropped significantly in the sixties, when they were replaced with zeolites in the cracking process. The oil crisis in the early seventies stimulated the investigation into the design of novel, large pore catalytic materials, and renewed the interest in clay minerals. As a result a new class of porous materials, known as pillared interlayer clays (PILCs), was developed, whose concept was a classical example of a nanotechnological approach to materials synthesis. Although successful application of PILCs in crude oil refining failed due to their relatively low hydrothermal stability, their investigation has been continued and the nineties saw a boom in synthesis, characterization and catalytic work on these materials. Currently most research into catalysis by PILCs is directed at tuning the catalytic properties to the requirements of a particular reaction by appropriate modification of the PILC structure, acid-base and/or redox functions.

An important stimulus for engineering new catalytic materials based on clays and layered silicates appeared in the early nineties, when it was discovered that the use of appropriate surfactant molecules as structure directing templates interacting with inorganic precursors allows for preparation of ordered mesoporous molecular sieves with uniformly sized channels of tunable diameter. This approach

was adopted in the synthesis of mesoporous materials from a layered sodium silicate named kanemite. The proposed formation mechanism was based on the idea of silicate sheet folding around the intercalated surfactant, hence the family of solids prepared in this way was called FSM (folded-sheet mesoporous materials). Another approach, which merged the concept of clay pillaring and the principle of surfactant-inorganic precursor self-assembly, led in 1995 to the preparation of smectite-derived materials known as porous clay heterostructures (PCHs). Ordered porous structures of the FSM and PCH types opened new opportunities for the design of catalytic materials and the number of papers on their application as catalysts or catalyst supports is rapidly growing.

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds or anionic clays, are considered the most promising precursors of mixed oxide catalytic materials. Their industrial application started with hydrogenation processes developed in the seventies. The advantage of using LDH-type precursors consists primarily in their structural flexibility, allowing for accommodation of a number of various elements within the layer and/or as interlayer compensating anions, thus providing a homogeneous mixing of components at an atomic level, unattainable with other preparative techniques. Depending on the adopted composition the LDH-derived catalysts are targeted at base or redox catalytic processes.

The talk is illustrated by authors' own works focused on environmental catalysis. The discussed fields of application include the end-of-pipe processes and green chemistry reactions.

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Clay minerals in the making

Javier CUADROS

Our common knowledge about clay mineral formation and transformation is frequently challenged by mineral assemblages that do not quite match our understanding of their formation conditions. Studies of clay mineral synthesis and of clay mineral formation or transformation in natural systems have provided results that indicate complex processes that result in an unexpected evolution of the clay mineral formation pattern or in the formation of complex, intermediate clay minerals. Some of the complexities observed in synthetic systems may derive from the short time scale involved and from other intrinsic features of these experiments. For example, synthesis in batch reactors is subjected to a change in the water chemistry as the reaction proceeds, which may cause changes in the clay formation pattern. However, these features may very well be present also in natural systems. Some examples will be discussed in the talk, among which are the following. In

which conditions is rock alteration (and clay mineral formation) controlled by the fluids or the rock? A case of clay mineral formation dominated by kinetic control. Transformation of clay minerals resulting in complex intermediates of the mixed-layer type and of a mixed di-tri-octahedral nature. Clay minerals are formed in a range of crystalline perfection and chemical composition so that the boundaries between “established” minerals may be blurred, for example in the sequences kaolinite–halloysite–smectite and talc–kerolite–smectite. Alteration promoted by living organisms may produce clay minerals different from those that the prevailing chemical and physical conditions would generate. The results from these examples prompt us to assess the quantitative relevance of such processes in natural environments and they may explain some of the irregular or complex clay mineral assemblages that we find in nature.

XRD texture measurements of oriented clay aggregates – a quantification tool

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Clay mineral quantification, although usually supplemented by information from other analytical techniques, strongly relies on XRD. XRD analysis of oriented clay aggregates generally involves empiric assumptions about the preferred orientation (texture) which controls the XRD intensity of clay minerals. Texture is expressed by the parameter σ^* and denotes the standard deviation of the tilt angles of 00l planes of the crystallites about their mean position once parallel to the surface of sample (REYNOLDS, 1989). The degree of preferred orientation depends on both type and morphology of the respective clay mineral. In order to increase the XRD detection limit the preparation of XRD texture slides produced by sedimentation on glass or ceramic slides (oriented clay aggregates) is frequently used. Ideally, oriented aggregates should exhibit perfect orientation of the clay mineral flakes parallel to the refracting plane. In this case, the standard deviation of the tilt angles of the crystallites about the mean crystallite orientation ('preferred orientation'), σ^* would be close to zero. Empirical considerations have led to propose a default value of $\sigma^*=12^\circ$ (REYNOLDS, 1986) for such instances where recorded diffraction intensities suggest preferred orientation to be typical for oriented aggregates. Peak intensity is proportional to $(1/\sigma^*)^2$, so the estimated limiting values for the reported σ^* -range from 4° to 30° will produce a 56-fold difference in basal or 00l intensities (MOORE & REYNOLDS, 1997). LIPPMANN (1970), ZEVIN & VIAENE (1990), and TAYLOR & NORRISH (1966) reported on preferred orientation of kaolinite varying between 8° and 20° for oriented aggregates and between 18° and 44° for powder samples. No σ^* results for smectites have been reported in the literature. The changes in preferred orientation cause very large differences in intensities. Therefore the use of "Mineral Intensity Factors" as discussed in KAHLE et al. (2002) is confirmed to be insufficient for the quantification of clay minerals in oriented aggregates.

68 mg of clay sample was dispersed in 1.5 ml of deionised water by ultrasonic treatment for 3 minutes at ultrasonic power of 32, 47, and 82 J s⁻¹. The clay suspensions were deposited on glass slides with a diameter of 2.4 cm and equally sized ceramic slides applying vacuum filtration. XRD measurements were performed using a Seifert 3003 TT diffractometer with an open Eulerian cradle, a 0.2 mm primary hole slit, a position sensitive detector (PSD)

and Cu K α radiation. The samples were rotated in $\phi=90^\circ$ increments, while χ was varied in 5° increments (70° maximum).

Na⁺ exchanged illite (<2 μ m) and Ca²⁺ exchanged kaolinite (<2 μ m) were used as standard materials. The σ^* values of the illite ($\sigma^*=14^\circ$ – 15°) and kaolinite ($\sigma^*=18^\circ$ – 19°) on ceramic and glass slide at different ultrasonic treatments are approximately the same. This indicates that the ultrasonic treatments had no significant influence on the preferred orientation of these two pure clay minerals. These pure minerals were mixed (80% illite, 20% kaolinite) and prepared on glass and ceramic slides. Results indicate that again there is no dependency of the σ^* values for kaolinite and illite for the type of slide used. However, there is a pronounced difference between the σ^* value of pure kaolinite ($\sigma^*=19^\circ$) and of kaolinite in the mixture ($\sigma^*=11^\circ$). The presence of illite influences the preferred orientation of kaolinite in such a way that kaolinite is forced to have a better orientation as observed by SEM. The trend was confirmed for mixtures with illite, kaolinite, and smectite. It can be concluded that there are no universal mineral intensity factors for clay minerals in oriented clay aggregates which limits their use for the quantitative analysis.

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Near infrared spectroscopy: a powerful method to learn more on modified smectites

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In the last years the growing interest in near infrared (NIR) spectroscopy has arisen from improvements in instrumentation and in data analysis as well as from the introduction of optical fibres allowing delivery and transfer of NIR energy and information. Among the advantages offered by NIR spectroscopy, the speed, the simplicity of the sample preparation and the non-destructive nature of the techniques are of great importance. The NIR region, covering the range between 12000–4000 cm^{-1} , contains bands corresponding to overtones and combinations of fundamental O–H, N–H or C–H vibrations. Consequently, NIR spectroscopy can also provide useful information about clay minerals since the bands related to the OH overtones and combination vibrations are sensitively affected by the variations in the clay mineral structure.

This paper demonstrates the potential of NIR spectroscopy to observe structural changes occurring upon various treatments of smectites. To follow migration of small exchangeable cations into the mineral layers and to study the effect of chemical composition of smectites, temperature of heating and the type of the interlayer cations on the layer charge reduction, series of reduced-charge smectites were analyzed. NIR spectra were obtained for Li-saturated montmorillonites, iron-rich beidellite and nontronite for unheated and heated (200°C for 24 hr to evoke Li-fixation) samples. No effect upon heating was found for beidellite and nontronite, while pronounced changes occurred in the NIR spectra of heat-treated montmorillonites. An upward shift and splitting of the OH overtone band at 7070 cm^{-1} into two components (near 7170 cm^{-1} and 7100 cm^{-1}) were observed. A band near 7170 cm^{-1} , assigned to the first overtone of the Al–Mg–Li–OH stretching vibration, proved creation of local trioctahedral domains as a result of Li fixation in the previously vacant octahedra. To investigate the effect of exchangeable cations on their fixation upon heating, series of materials were prepared from Li⁺- and Ni²⁺-saturated montmorillonite by heating for 24 hours at different temperatures. The NIR spectra confirmed that both the size and the charge of interlayer cation affect their final position after fixation upon heating. Though Ni²⁺ has similar ionic radius as Li⁺ no spectral features demonstrating its presence in the octahedral positions were found even in sample heated at 300°C. Ni(II) is supposed to be fixed

deep in the ditrigonal cavities of the tetrahedral sheets of montmorillonites.

The alteration of the smectite structure upon acid treatment has been traditionally studied by spectroscopy in the middle IR region. An upward shift of the Si–O stretching band (~1030 cm^{-1}) along with gradual decrease in the intensity of the OH (950–800 cm^{-1}) and Al–O–Si (~525 cm^{-1}) bending bands revealed decomposition of the layers as the extent of dissolution progressed. NIR spectroscopy, however, is also well suited for monitoring the reducing content of octahedral cations by gradual decrease of the OH overtone band (~7070 cm^{-1}) intensity. Moreover, this region offers new information on creation of Si–OH groups in the course of acid dissolution. The increasing intensity of the Si–OH overtone band near 7315 cm^{-1} indicates transformation of layered structure to a partly protonated amorphous silica phase. The effect of chemical composition and layer charge on structural modifications of various dioctahedral smectites was investigated. NIR spectra proved that with increasing octahedral Mg content the resistance of montmorillonites against acid attack decreased. OH overtone region of acid-treated reduced-charge montmorillonites showed that a layer charge decrease connected with a development of non-swelling interlayers substantially affected their dissolution in HCl. The spectra of unheated Li- and Ni-montmorillonites revealed a substantial degradation of the structure and progressive formation of protonated amorphous silica. The sensitivity of the MIR spectroscopy to follow leaching of the octahedral atoms from unheated smectites was higher than that of NIR spectroscopy. On the other hand the Si–OH overtone near 7314 cm^{-1} reflected of the extent of acid attack of smectites even in the case when no differences were observed in the 1300–400 cm^{-1} spectral region, traditionally used to monitor this process. Development of non-swelling interlayers substantially restricted the access of protons to the layers and the extent of the acid attack was reduced. The results confirm that acid attack of the smectite structure occurs at both interlayer surfaces and edges. If the accessibility of the layers for protons was low due to non-swelling interlayers, the dissolution was slower and took place mainly from the particle edges.

Mössbauer spectroscopy of geological materials

Enver MURAD

Many branches of the basic and applied sciences make use of physical techniques such as X-ray diffraction and various spectroscopic techniques. One of the most powerful of the latter is Mössbauer spectroscopy, the technique of recoil-free resonant emission and absorption of gamma rays.

Mössbauer spectroscopy has the advantage of being oblivious to all elements except that under survey. In the case of materials formed on the Earth's surface (*i.e.* in the weathering environment), the only propitious element is iron. Iron is the fourth most abundant element in the Earth's crust, it is essential for life, and almost all environmental materials contain iron in varying concentrations. It is thus fortuitous that ^{57}Fe is one of the most convenient nuclides for Mössbauer spectroscopy. ^{57}Fe Mössbauer spectroscopy allows a quantitative determination of the oxidation state(s) of iron and the identification of magnetically ordered phases (generally iron oxides and oxyhydroxides in samples formed in the weathering environment), *i.e.* the characterization of iron speciation – and thereby of environmental conditions – over a wide range of concentrations, and is consequently an effective environmental probe (MURAD & CASHION, 2004). Thus Mössbauer spectroscopy can be used to characterize the iron-bearing constituents of clays, soils and sediments, it has been successfully applied to the study of

weathering reactions, and it has recently been used as an *in-situ* probe on Mars. Metastable phases can be studied by taking spectra under protective environments or by cooling samples to temperatures at which their transformation would essentially come to a standstill. Samples of complex mineralogy may require pretreatments such as particle size fractionation or selective iron oxide removal prior to measurement, and/or more sophisticated techniques such as the application of external magnetic fields.

In my lecture I will give enough introductory information on the theory to provide a background for understanding the principles behind the measurements. I will then present a description of the properties of selected materials formed on the Earth's surface, their synthetic analogs where applicable, and the products of their modification in the course of natural processes or in processing as reflected in their Mössbauer spectra. This will be complemented by remarks on the current status of lunar and planetary studies using Mössbauer spectroscopy.

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New insight into halloysite physico-chemical properties

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Halloysite is a 1:1 clay mineral that occurs widely in both weathered rocks and soils developed on volcanic ash. Halloysite is the only kaolin mineral found as a natural hydrate. Because the interlayer water is highly labile when the halloysite sample is left standing in dry air, vacuum, or heating, halloysite-(10Å) is very susceptible to dehydrate irreversibly, producing the dehydrated polymorph known as halloysite-(7Å). The interlayer water of halloysite seems to play an important role in the physical properties of this mineral, its exchange properties, and its reactivity when in contact with organic species (JOUSSEIN et al., 2005). It is thus very important to fully understand the hydration–dehydration behavior of halloysites for a variety of industrial or environmental applications. However, it is extremely difficult to study halloysite-(10Å) without inducing some alteration in its hydration status. In this work, we will show you the actual morphology of hydrated spherical halloysite (halloysite-10Å) and its change under vacuum induced dehydration by transmission electron microscopy (TEM) using an environmental cell under water saturated flux and vacuum.

To study the dehydration behavior of several types of halloysite (tubular, spherical), some reference halloysites were studied by X-ray diffraction (XRD) under various relative humidity (RH) and various temperature. They were also studied by thermal analyses at 40 and 0.2% RH. For each halloysite sample, the decrease in RH and the increase in temperature induce similar dehydration behavior regardless of the size fraction, but the dehydration processes are not the same for all samples. For some of them, the dehydration proceeds with one intermediate hydration state reacting as a separate phase due to the presence of “hole” water molecules. On the other hand, the dehydration of an initially fully hydrated halloysite gives a dehydrated phase with the presence of a 8.6–7 Å mixed-layer at 7.9 Å. The results show that the presence of different types of water molecule, the “associated” and the “hole” water, controls the dehydration behavior of halloysites. Moreover, the rehydration experiments at 95% RH after dehydration at 0% RH only result in a partial rehydration.

Halloysite is also of interest for soil fertility in tropical countries due to (i) its possible cationic exchange capacity (CEC), which can be relatively high (20–50 cmol_c kg⁻¹ in halloysitic soils) and (ii) its possible selectivity for poorly hydrated cations, such as NH₄⁺, K⁺ and Cs⁺. However, the origin of the charge as well as the presence of interlayer cations have never been evidenced in halloysite. In regard to this topic, some halloysite samples were selected: two “low-charge” reference halloysites, namely Te Puke and Matauri Bay, and a “high-charge” fine clay SN2 halloysitic sample (<0.1 μm) from a Cameroon soil. Samples were submitted to (i) K-saturation, and (ii) K-saturation, washing and Ca-saturation. The samples were studied by XRD, FTIR, MAS-NMR (²⁷Al and ²⁹Si), and Mössbauer spectroscopies. The chemical compositions of individual particles were determined by TEM-EDX. For all samples, K selectivity and CEC were measured before and after heating samples at 100°C/8hr. K selectivity as well as CEC strongly decrease after dehydration of sample. The low-charge Te Puke is more selective for K than the high-charge SN2; Matauri Bay being far less selective. Chemical analyses of single particles by analytical electron microscopy revealed relatively large amount of K in Te Puke and SN2 halloysites particles. A part of K is still remaining after Ca-saturation and is thus non exchangeable by Ca²⁺. These results reveal the presence of K-specific sites in halloysites. No charge due to ^{VI}Al/Fe²⁺ or Si/Fe³⁺ substitutions could be evidenced by Mössbauer spectroscopy. However, NMR data reveal that some ^{IV}Al occur in the studied halloysites which can be responsible for the CEC measured from the dehydrated samples. A hypothesis concerning the change of physico-chemical properties of halloysite after dehydration will be proposed.

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Clay mineralogy, petrography and geochemistry of Late Palaeozoic siliciclastic rocks from the Mecsek–Villány area (SW Hungary): implications for source-area weathering, provenance and diagenesis

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Sandstone geochemistry is widely considered to be a powerful tool for determining the sediment source areas and tectonic settings of ancient terrigenous deposits. Whole-rock chemistry can also detect variations in elements that are not picked up in modal analysis, for example rare earths elements (REE), Th, Zr, Sc, and Cr. In addition, variations in clay-mineral assemblages also may be useful for detecting changes in the source areas and for recognizing the diagenetic conditions of sandstone units. On the other hand, relatively few papers deal specifically with clast composition of coexisting conglomerates in the same locality; however, the clast types can provide a wealth of information concerning the provenance and geological evolution of the sediment source areas. Therefore, integrated examination of siliciclastic rocks, including clay mineralogy, whole-rock geochemistry, and clast petrography and geochemistry, is particularly fruitful in provenance analysis and paleogeographic reconstruction.

In this work, results of clay mineralogical, petrographic and geochemical studies of the Late Paleozoic siliciclastic successions from southern Transdanubia (Mecsek–Villány area, Tisza Mega-unit, SW Hungary) are presented.

The Paleozoic formations studied in this paper are the Téseny, Korpád, and Cserdi formations. The Téseny Formation (Upper Carboniferous), which is interpreted as fluvial system deposits, unconformably overlies the crystalline basement and has a maximum thickness of ~1500 m. This formation is found partly in the western flank of the Villány Mountains and also in the Drava Basin. It is composed of conglomerate, sandstone, and siltstone; in addition, shale and coal seams also occur. The alluvial Korpád Formation (Lower Permian) ranges up to 700 m in thickness and consists of polymictic basal conglomerate, breccia, sandstone, siltstone, and claystone. However, extreme variation in thickness has been documented. The Cserdi Formation (Upper Permian) consists of up to 1000 m of polymictic conglomerate, sandstone, and siltstone beds representing debris flow-dominated alluvial fan deposits.

The Upper Carboniferous/Pennsylvanian Téseny Formation consists of relatively metamorphic lithic-rich sandstones with a combined recycled-orogen, basement-uplift,

and volcanic-arc provenance. Low-grade to medium-grade metamorphic source components might be derived from local sources in the Baksa Subunit. The inferred sources of fine-grained plutonic rocks are microgranite dikes of the Mórág Complex (Kunság Unit). The high median of SiO₂ and low Na₂O, CaO, Sr, high field strength elements (HFSE), and REE contents in this formation reflect that source rocks were more mature than those which supplied detritus to the Permian strata. Our data also indicate a more intense weathering in the source region. Additionally, high medians of K₂O and Rb, together with the presence of abundant illite/sericite suggests a potassium metasomatism in the Téseny clastics. Characteristics of the Lower Permian Korpád Formation vary spatially, and are interpreted as local variations in composition of the source areas and diagenetic conditions. Relatively immobile trace element relations, however, clearly show that this formation was mainly derived from mature upper continental crust. Korpád-A group represents combined acidic–intermediate volcanic and basement-uplift provenances. A possible source for this group is the Carboniferous granitoid basement in the western Mecsek Mountains. On the other hand, the provenance of the Korpád-B group represents sources exclusively from the uplifted Baksa-type metamorphic rocks. The petrographic, clay-mineralogical and geochemical features of the Upper Permian Cserdi Formation, especially the presence of abundant acidic volcanic fragments and chlorite, together with the high TiO₂, Th, U, Y, and Cr contents, and evolved HREE pattern relative to the underlying formations, may reflect relatively proximal derivation from a felsic volcanic source. It may be possible to link huge amounts of felsic detritus in Cserdi sediments to the Gyűrűfű Rhyolite Formation. These upward variations to less mature deposits might be related to such factors as increasing aridity and favoring conditions of weathering-limited erosion in the source regions, and the increase of tectonic activity including intense acidic volcanism during the Early Permian rifting in the southern margin of the European plate.

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Clay-based bionanocomposites

Eduardo RUIZ-HITZKY

Polymer–clay nanocomposites refer to nanostructured materials in which synthetic polymers are assembled to clay minerals interacting at the nanometer level. These materials have been largely studied in view of their structural or functional properties (RUIZ-HITZKY, 2004). Bionanocomposites are an emerging group belonging to the polymer–clay nanocomposite family in which the involved polymers are of natural origin (biopolymers) (RUIZ-HITZKY et al., 2005, 2006). Polysaccharides, proteins, enzymes and nucleic acids are examples of these biopolymers involved in the assembling with different smectites, layered double hydroxides (LDHs) and also with sepiolite. The incorporation of proteins provided of functional behaviours (enzymes) to smectites, as well as the intercalation of DNA and related macromolecules in LDHs are examples of the development of bionanocomposites, regarded in some cases as biomimetic materials.

Cationic biopolymers such as chitosan in a slightly acidic medium act as a positively charged polyelectrolyte leading to intercalation compounds with smectites (DARDER et al., 2003, 2005a) (Fig. 1). In a similar way, anionic polysaccharides such as pectin, alginate and carrageenan can intercalate LDHs giving the corresponding bionanocomposites (DARDER et al., 2005b). By controlling the amount of intercalated chitosan it is possible to reverse the cation exchange ability of the starting smectites in an anion exchange ability in the resulting bionanocomposite. The opposite behavior for the LDH derivatives is found after combination of this solid with anionic biopolymers. On the other hand clay minerals, such as sepiolite, appear also as suitable inorganic moieties for biopolymer–clay nanocomposite preparations (DARDER et al., 2006) (Fig. 2).

The resulting hybrids can be classified as *green nanocomposites* within the so-called ecomaterials group because they exhibit the ecological properties inherent to both components, i.e. clays and natural polymers, showing improved mechanical behaviours compared to the individual components, together with functional properties associated to the ion-exchange properties determined by the clay and the ionizable biopolymers.

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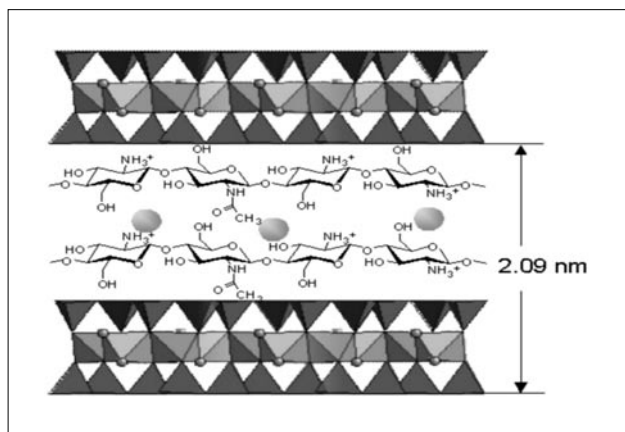


Fig. 1 Chitosan–montmorillonite bionanocomposite in a bilayer conformation.

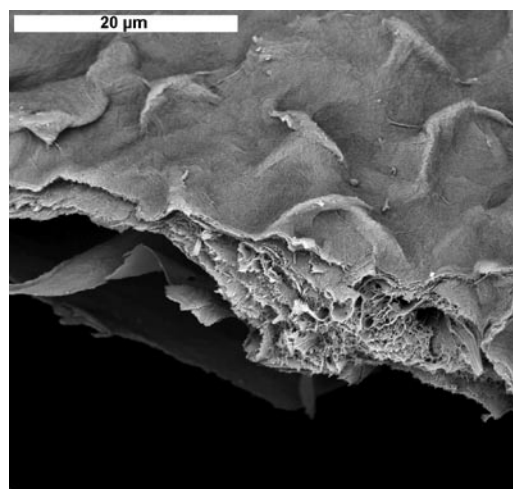


Fig. 2 SEM image of a sepiolite–chitosan bionanocomposite.

Zeolite deposits in Croatia

Darko TIBLJAŠ and Stjepan ŠČAVNIČAR

In spite of the fact that zeolites have been found at several locations in Croatia, so far only two regions with economically interesting concentrations are known. Both are situated in northern part of the country i.e. in the part that belongs to the Pannonian Basin.

The first one is located in the Macelj area in north-western part of Hrvatsko Zagorje (NW Croatia) in which Lower Miocene (Egerian–Ottangian) volcanoclastic rocks, up to 100 meters in thickness, have been described on several localities. They occur in several horizons interbedded with shallow-sea clastic sediments within the elongated syncline which gradually sinks towards the east (ŠIMUNIĆ et al., 1995). They have variable primary composition, and contain various alteration products of volcanic glass. The alteration products comprise zeolites, clay minerals (smectite, authigenic mica), SiO₂ phases and authigenic feldspars. Clinoptilolite is the most abundant zeolite, however analcime and mordenite are also present. The type of exchangeable cations in clinoptilolite is variable; therefore clinoptilolites were divided into three subgroups: Ca-rich, Ca-K, and Na-rich. Clinoptilolite content in the volcanoclastic rocks discovered in Macelj area vary significantly, in some rocks it is the dominant component, in others it is present only in traces. In Donje Jesenje quarry, in which due to exploitation the best outcrops of these rocks can be found, the variations, although present, are not so conspicuous, and the average content of clinoptilolite is approximately 50 wt. %. Alteration of volcanic glass is the result of burial diagenesis. Different alteration products are most probably due to different temperatures to which sediments were exposed, with increasing depth of burial clinoptilolite transformed to mordenite and analcime, while opal-CT changed to opal-C and recrystallized to quartz. However different immobile element content of rocks containing different alteration products indicates that alteration was probably also dependent on chemical composition of the rocks. Some types of alteration product were also dependent on chemi-

cal composition of primary material and its granulometric characteristics. Huge reserves of volcanoclastic rocks make them economically interesting, nevertheless it will be necessary to take care about raw material properties i.e. zeolite content and its chemical composition, when planning its particular application.

The other deposit is located in Slavonian Mountains, on the southern slopes of Mt. Papuk in the vicinity of village Poljanska in Požega Valley (ŠČAVNIČAR et al., 1983). In the deposit four horizons that are results of changes in climate and related variations in sedimentary basin characteristics can be differentiated; two with analcime-bearing rocks (used in cement industry) which are underlain by sandy calcareous shales and separated by marly horizon. The analcime-bearing rocks are of hybrid composition. They contain, in layered or laminar alternation or mixed together, in various proportions, authigenic dolomite, volcanoclastic and pyroclastic particles from neighbouring ancient volcanoes as well as terrigenous psamitic and pelitic material. The analcime, that is present as dispersed grains or in monomineral laminae and thin layers, was formed by alteration of pyroclastic material within closed hydrological system i.e. shallow saline alkaline lake which existed during early Miocene (Ottangian) time due to arid and semiarid climates. The conditions in such lake were also favourable for formation of dolomicrites. On the contrary calcareous footwall and marly interhorizon were deposited during more humid climates in a lake characterized by fresh water.

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Engineering properties of clays

Dobroslav ZNIDARČIĆ

Clays and other materials containing clay minerals are ubiquitous and they are routinely encountered in many engineering projects. They are found in naturally occurring clay layers, in mining and dredging operations, in the ceramic industry and in all other activities that involve earth materials. In all these instances the engineering properties of clays should be known in order to predict the behavior of the material and to quantify its response to various loading conditions. Deformation, hydraulic conductivity and strength characteristics are the essential properties and must be determined with a reasonable level of cer-

tainty. They depend on the clay consistency and cannot be considered invariable for a material. The paper discusses testing methods used to determine these characteristics and investigates the range of values encountered in various projects. The examples of projects in which the engineering properties are used to predict the field behavior include mine waste disposal, dredging operations, deep sea foundation anchors and the manufacturing process in the ceramic industry. In all instances the critical element for a reliable prediction of the field behavior was the determination of the engineering properties of clays.

Abstracts

Waterproof polymeric heat insulators based on clay fillers: mechanical properties

Basim ABU-JDAYIL and Kamal AL-MALAH

Introduction

There is an ongoing search for finding the proper alternatives to preserve energy and minimize energy losses. Our country, like other countries, highly appreciates all forms of energy saving, taking into account that Jordan faces a shortage in renewable energy resources. Subsequently, heat insulators, part of building materials and some industrial hardware, are steadily getting their importance as a means of saving energy. Heat insulating materials available in the local market are relatively expensive and until now are scarcely used by local contractors and small-size entrepreneurs. In this research, focus is made on the formulation of polyester–clay composite as an insulating material that gives the best in terms of thermal and mechanical properties. Different types of local fillers were used in the formulations. In this paper, the effect of filler type and content on mechanical properties of the composite is presented.

Experimental methods

The type of polyester used is HM190 with a styrene content of 33–35%, an acid content of 21–23% and a viscosity of 300–400 mPa.s. Clay samples obtained from different areas in Jordan were used in this study as fillers. Different filler contents (25–60 wt%) at a constant styrene/polyester ratio (18 wt%) and different styrene contents (5–12 wt%) with constant filler content of 50 wt% composites were prepared. The composites were prepared at room temperature using a high viscosity mixer. The different mechanical tests were performed according the ASTM standards for composites and ceramics.

Results and discussion

From the experimental work performed in this project, we concluded that the natural clay (bentonite and feldspar) can be utilized to manufacture stable and compatible composite materials. An interesting point obtained from the results, important from a technological and commercial point of view, was that for all filler types the addition of the clay filler to the polyester composites improved the mechanical properties of the polyester composite and lowered its cost. Only if the filler content was higher than 60% wt the product formulation was found to be inconsistent and non-reproducible. In most cases, the mechanical

properties of the composites depended on the filler type, filler content and, to a lesser degree, on polyester content. The prepared samples resisted relatively high bending and compressive forces. The bentonite fillers with the highest content of Al_2O_3 possessed the greatest bending and compressive forces. In most cases, the mechanical strength of the composites increased with filler content to reach a maximum value, and then it decreased again. It seems that the mechanical strength increase with increasing clay content was a result of the catalytic effect of clay constituents. It should be recalled that the bentonite is a type of clay mainly composed of montmorillonite that is a 2:1 type aluminosilicate. It has a crystalline structure with an octahedral layer of aluminium hydroxide between two tetrahedral layers of silica (ALLAOUI et al, 2002). The increase in bentonite content in the composite increased the amount of the aluminosilicate which has a catalytic effect on the co-polymerization rate of the unsaturated polyester/styrene mixture in which a large number of cross-linking occurred which resulted in an increase in the mechanical strength (ISMAIL et al., 1999). Also, increasing bentonite content has increased the amounts of MgO and CaO that reacted with the acidic groups of the unsaturated polyester resin to form a dense network structure in the presence of styrene. For a composite with more than 40 wt% bentonite the specimens showed a decrease in its mechanical strength due to the relatively high viscosity of composite, which decreased the impregnation process of bentonite into the polyester.

The tensile strength of all composites was lower than the compressive strength, but it was one order of magnitude greater than that of the commonly used insulating materials. However, one of the bentonite composites and feldspar composites were somewhat distinguished with their tensile strengths, which are due to their high content of Al_2O_3 and SiO_2 .

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Latvian smectite clay and bentonite interaction with tetraoctyl-ammonium bromide

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Sorption properties of clays have been used and studied a lot, but still it has not been established, how organic surfactant cations take positions in organoclay's basal space (LAGALY & MERMUT, 2001).

Latvian smectite clay and bentonite (Kazakhstan) interact with tetraoctyl-ammonium bromide (TOABr) – change of basal spacing in organoclay proves it. Swelling of clay is noticeable already by small proportions of TOABr and clay (as of 0.05 mmol TOABr per 1 g clay). Normally sorption of surfactant is limited by cation exchange capacity (CEC) – for bentonite CEC is 0.8–1.0 mgeq/g (JASMUND & LAGALY, 1993). TOA cation is different – saturation is shown when proportion of TOABr and clay exceeds 0.5 mmol/g. Latvian smectite clay (after hydroclassification using tetrasodium pyrophosphate) just like bentonite is Na montmorillonite, but their corresponding organoclays have different maximum basal spacing.

Both Latvian TOA smectite clay and TOA bentonite have poor sorption properties – they practically do not swell in interaction with alcohols and hydrocarbons.

TOA cation is forked, its dimensions oversize area of inorganic cation, wherewith exchange of all inorganic cations is impossible. When the maximal packing of TOA cations in organoclay is reached, there is no free space for alcohols and hydrocarbons between hydrophobic tails of TOA cation.

It is experimentally established that bentonite and Latvian clay have different layer charge – that is the reason of various basal spacing. Latvian smectite clay is heterogeneous – during the formation of organoclay sequentially appear phases with various packing. Active phases with most dense packing are minority; they can adsorb not only TOA cations, but TOABr as salt too; specific structural transformation is shown. This way basal spacing can increase up to 40 Å.

Theoretically TOA cation can be situated in several positions. - Fig. 1 shows some examples of them. Using geometrical formulas theoretical size of TOA cation and basal spacing can be calculated. Calculated maximal basal spacing (see Fig. 1 (c)) is 26 Å. Experimentally acquired maximal basal spacing is 23.4 Å (bentonite) and 27 Å (Latvian clay). Most probable position of TOA cations is shown in Fig. 1 (b) – hydrophobic chains interlace dense together filling out space, though not allowing to squeeze other molecules in.

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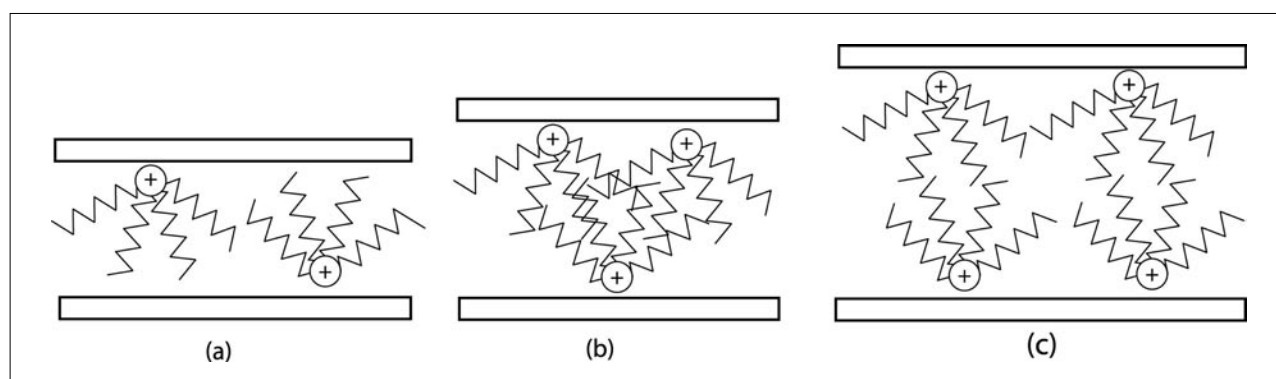


Fig. 1 Theoretical positions of tetraoctyl-ammonium cations between layers.

Engineering geological research of highly compacted bentonites in Slovakia

Renata ADAMCOVA, Zuzana HAASOVA and Peter MAAS

Article summarizes the experience from the research on physical parameters of bentonites for their use as buffer material in the barrier system of the planned deep geological repository for the radioactive waste. Bentonites from 5 different deposits in Slovakia have been tested. However, due to the research contract, we are not allowed to give information about the deposits, neither the exact mineralogy, nor the chemistry of the bentonites. Natural bentonite was industrially dried, crushed and 3 different fractions (<0.250 mm, <0.045 mm and <0.015 mm) were separated using cyclone. One of the bentonites was also natrified by adding 4% of sodium-hydroxide.

First of all, the Atterberg's consistency limits have been tested, as they can tell much about the sorption and swelling capacity of the clay. Because a high swelling pressure is needed, causing the closing of any cracks and failures in the barrier (so-called "self-healing" effect), the sample with the highest liquid limit would be the most promising one. We applied two methods: the Cassagrande apparatus and the cone penetrometer method (BS 1377, 1990). However, the liquid limit of the natrified bentonite was already too high (>600%!), higher than reported for MX-80 (STUDER et al., 1984). The natural bentonite with the highest content on exchangeable sodium yielded 160 to 190% and the best Ca-bentonite 100 to 158%, according to the grain size, which is similar to the Montigel bentonite tested in Switzerland (STUDER et al., 1984). Finer samples show higher liquid limits. Presented values are results from the Cassagrande apparatus. Cone penetrometer test gave always lower numbers.

Bentonite will be probably applied in the form of pre-fabricated high-density segments. Dry densities of 1.8 to 2.0 g.cm⁻³ are required. Therefore, the compactibility of the bentonite powder was the second most important question. Because the Proctor Standard compaction method (i.e. compaction of wet soil in a mould with a rammer) never yielded such high values of the maximum dry density, specially designed moulds and a high-capacity hydraulic jack were applied for pressing high-density bentonite cylinders, 50 mm in diameter and ca. 50 mm in the height. Curves of the necessary uniaxial pressure versus reached dry density have been constructed, that allowed a quantitative comparison. However, the quality of the pressed cylinders had to be considered, as well. We saw that the quality decreased and the pressure increased with the increasing content of both, the fine fraction and the sorbed atmospheric water vapour in the sample. The coarse frac-

tions (<0.250 mm) yielded always the highest dry densities. The effective porosity is higher there, which allowed the air to escape from the pores during pressing. The air remaining in the very small pores in the finer fractions behaves as an elastic material requiring higher pressures for pressing bentonite to similar densities. In the finest fractions (<0.015 mm), the necessary pressure (up to 200 MPa) was so high, that the sorbed water was pressed out from the sample. This caused sticking of the wet bentonite surface to the mould and increased the friction leading to the shear stress and occurrence of shear failures (cracks) in these samples. Unfortunately, the best bentonites (with the highest content of smectite) sorb the highest amount of the atmospheric water vapour. Therefore, we have definitely left the finest fractions (<0.015 mm) and preferred the coarser ones, where the risk of cracking is reduced.

Preferably coarser fractions have been used also for pressing standard-shaped samples for mechanical tests (cylinders, cubes). We tested the uniaxial pressure strength that yielded values similar to rocks or weak rocks eventually (from 1 to 10 MPa). Here, the sorbed water vapour seems to contribute to the cohesion. Therefore, certain water content is necessary for higher strength. Samples pressed from an oven-dried bentonite behaved as cohesionless soils and lost their form by a simple manual manipulation. Therefore, segments pressed from bentonites with higher smectite content (i. e. higher equilibrium moisture) seem to be more suitable. There are still not enough results about the deformation moduli there, but this research goes on. The shear strength has not been tested yet.

Finally, swelling pressure was tested in consolidometers. One of the bentonites shows results very similar to the FEBEX bentonite (www.grimself.com/febex), when an exponential trendline was drawn into the chart of the relation between the dry density and the swelling pressure. A free-swelling test followed. The hydraulic conductivity was calculated next from the consolidation curve. Already at relatively low densities of about 1.3 g.cm⁻³, the hydraulic conductivity of the most perspective bentonite did not exceed 6.2·10⁻¹² m.s⁻¹.

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Clay mineralogy in northern Iraq during the Miocene: paleoenvironmental indicators

Ali AL-JUBOURY

Introduction

The Miocene sedimentation of northern Iraq is characterized by the marine nature and was started by deposition of early Miocene carbonates and evaporates of Serikagni, Euphrates, Dhiban and Jeribe formations within shallow epicontinental seas and lagoons in marginal basins. Marine conditions became progressively more restricted, with many small seas and lagoons sporadically replenished with normal marine water. These gave rise to the shallowing-upward cyclic deposition of evaporates in middle Miocene (Lower Fars, Fat'ha Formation – NUMAN, 1997). In the marginal parts of Fat'ha basin the clastics dominate and are represented by fine sandstones and silty claystones occupying the upper two-thirds of the sequence of the upper unit of the formation and characterized by red coloration. These clastics were interpreted to be deposited in fluvial-dominated deltaic system (AL-JUBOURY et al., 2001). The deposition of fluvial Injana Formation in the foreland basin of Iraq in the Upper Miocene marked the end of marine conditions in northern Iraq. This formation is a clastic sequence of medium to coarse sandstones, siltstones and claystones and deposited in fluvial-tidal environment (AL-JUBOURY, 1994). Clay mineralogy of the Miocene successions taken from northern Iraq constitutes an important paleoenvironmental indication for the evolution of these sediments.

Results & Discussion

The principal clay minerals present include; kaolinite, illite and palygorskite. Palygorskite is a common mineral especially in the lower Miocene sediments of Euphrates formation and the upper detrital part of the Fat'ha Formation belonging to the middle Miocene. Scanning Electron Microscope (SEM) study indicated that this mineral was formed authigenically by neof ormation in suitable chemical conditions within the evaporitic environments. Other minerals (kaolinite and illite) had been most probably formed in detrital system and were preserved in those evaporitic conditions. Common kaolinites in the Injana clastic Formation (upper Miocene) as well as its habit in SEM images are indicators for its detrital origin in such continental sediments.

Scanning electron images show the well defined pseudo-hexagonal plates of the studied kaolinite especially those taken from the Injana continental samples (Figure 1A). Illite appears as white flakes in carbonate cemented sandstones (Figure 1B). Illite is a common mineral in the studied samples. This mineral existed in the older Tertiary and Cretaceous successions from northern Iraq. Palygorskite is a fibrous clay mineral and is commonly associated with dolomite and other Mg-rich minerals. CHAMLEY (1989) has shown that palygorskite derives from chemical precipitation in evaporative basins. He summarized the conditions for palygorskite formation as "alkaline conditions in restricted basins subject to marine transgression, limited water exchange, warm and humidity, contrasted climate and strong evaporation". It seems that evaporative conditions are suitable for the formation of palygorskite as neoformed clay mineral in restricted back-reef and lagoons of the marl beds of the Euphrates Formation. SEM photomicrographs show palygorskite as long and small fibers indicating their authigenic origin (Figure 1A, C & D).

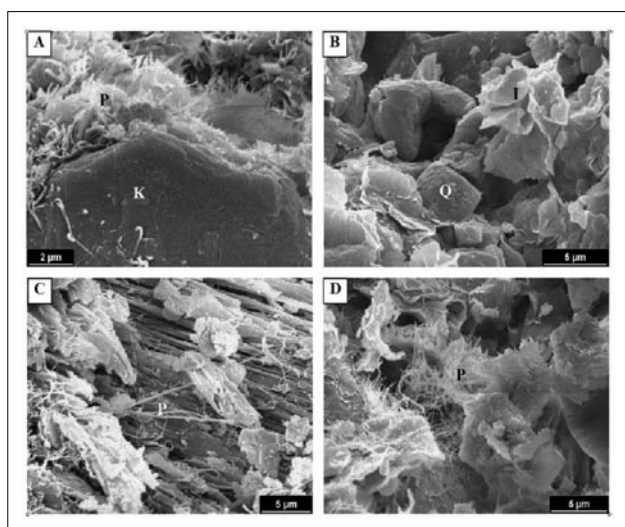


Fig. 1 SEM images showing the morphology of the observed kaolinite, illite and palygorskite. Legend: K=Kaolinite, I=Illite, P=Palygorskite and Q=Quartz.

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Phase composition and geotechnical evaluation of bentonite from Lieskovec, Slovakia

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Powder XRD and IR spectroscopy were used to identify mineralogical composition of the bentonite samples from the Lieskovec deposit (Central Slovakia), developed from andesitic pyroclastics. The main mineral is a montmorillonite, the admixtures present in all samples include kaolinite, quartz, cristobalite and plagioclase, while muscovite/illite and orthoclase appear in most samples. This bentonite deposit is relatively homogeneous. Detailed analysis of the infrared spectra shows that the dominant mineral in the samples is a Fe–montmorillonite with rather low isomorphous substitution in the octahedral (Mg^{II} for Al^{III}) and tetrahedral (Al^{III} for Si^{IV}) sheets (ANDREJKOVIČOVÁ et al., 2006).

Basic geotechnical properties of ten bentonite samples are reported in Table 1. Differences between the lowest and highest values of plasticity and liquid limits are 26.2% and

16.2%, respectively. Free swell tests of 3–6% are typical for Ca–bentonites. All ten bentonite samples are characterized by low water sorption capacities (w_p , w_L , E_s and free swell test). Permeability coefficients of L1, L15 and L22 are of the order of 10^{-11} m.s⁻¹, what is the primary requirement for using of bentonite for sealing purpose. k_{20} –values of these samples differ only slightly, and are primarily dependent on the smectite content. Based on these results, bentonite from Lieskovec deposit is a promising material to be used after natrifcation as a sealing material in a function of geosynthetic clay liner.

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Table 1 Geotechnical properties of bentonite samples from the Lieskovec deposit.

Property	L1	L4	L5	L8	L11
Plasticity limit w_p (%)	47.4	34.6	33.2	44.3	47.8
Liquid limit w_L (%)	73.2	80.4	64.2	72.1	80.1
Plasticity index I_p (%)	25.8	45.8	31.0	27.8	32.3
Water adsorption Enslin E_s 24 h (%)	236.2	123.2	126.5	363.2	605.9
Free swell test (%)	4	4	5	5	6
Coefficient of permeability k_{20} (m.s ⁻¹)	2.4×10^{-11}	–	–	–	–
Property	L12	L15	L20	L22	L26
Plasticity limit w_p (%)	59.5	44.2	42.5	42.6	42.2
Liquid limit w_L (%)	76.2	75.5	72.3	67.2	66.3
Plasticity index I_p (%)	16.7	31.3	29.8	24.6	24.1
Water adsorption Enslin E_s 24 h (%)	312.4	259.0	163.1	166.3	316.5
Free swell test (%)	5	5	3	4	4
Coefficient of permeability k_{20} (m.s ⁻¹)	–	2.1×10^{-11}	–	2.7×10^{-11}	–

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TiO₂/delaminated-clay nanocomposites

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Nanostructured solids based on layered silicates of the smectite family are materials of increasing interest based on both structural characteristics and functional applications. Among them polymer-clay nanocomposites are probably the most studied (PINNAVAIA & BEALL, 2000). A new type of nanocomposite materials based on smectites and other clays in which delamination of the layered silicate is accomplished by incorporation of a silica matrix generated from the hydrolysis of alkoxy silanes, has been recently reported by our group (LETAIËF & RUIZ-HITZKY, 2003). These inorganic-inorganic nanocomposites are prepared by a colloidal route that implies the use of organo-clay derivatives in which the silane precursor is first incorporated and further hydrolyzed giving materials that show interesting textural and ion-exchange properties (LETAIËF et al., 2006). Considering that TiO₂, specially in the anatase phase, is a very efficient photocatalyst for decomposition of organic pollutants (ANPO, 2000; FUJISHIMA et al., 1999) and that titania-clay or titania-silica materials appear to provide a solution for such problems (LI et al., 2002; NÉMETH et al., 2003; ZHU et al., 2005), we have developed new inorganic-inorganic nanocomposites following the approach for the synthesis of silica-clay systems but using titanium alkoxyde precursors instead. The objective is to obtain materials incorporating nanosized TiO₂ anatase particles provided of relatively large specific surface area but not agglomerated, which are expected to be useful in view of their catalytic properties. This communication will introduce results concerning the preparation and characterization of titania/ and titania-silica/clay materials prepared by this route as well as some of the photocatalytic properties of the resulting nanocomposites using the reaction of photodegradation of 2,4-dichlorophenol as a test.

Standard Wyoming montmorillonite (SWy-1) from County Creek (Wyoming, USA), an iron-rich smectite from Gafsa (Tunisia), and vermiculite from Benahavis (Málaga, Spain) were the clays chosen for delamination and incorporation of dispersed TiO₂ nanoparticles. Organically modified clays were prepared by treatment with cetyltrimethylammonium bromide and delamination was intended in isopropanol media following the procedure

previously described (LETAIËF et al., 2006), using titanium isopropoxide or titanium isopropoxide/tetramethoxysilane mixtures slowly hydrolyzed till formation of homogeneous gels. Heating at 500°C in air remove the organic matter giving TiO₂-clay derivatives that were characterized by means of XRD, FTIR, thermal (TG-DTA) and chemical analyses, specific surface area and porosity determinations, TEM, SEM-EDX and ²⁹Si NMR techniques. These studies confirm the formation of nanocomposites consisting in anatase TiO₂ nanoparticles homogeneously dispersed in delaminated clays. These inorganic-inorganic nanocomposites show higher surface areas and porosities than their individual counterparts (clays and TiO₂ separately) indicating the potential interest of these systems as catalysts. Photocatalytic test of 2,4-dichlorophenol decomposition in aqueous solution show activities and kinetics of the decomposition processes comparable to that of commercial P25 anatase, having two-fold activities per unit mass for the nanocomposites here developed.

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Mineralogy of a Carboniferous bentonite from the Sudetes (SW Poland), northern margin of the Bohemian Massif – preliminary data

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It is well recognised that bentonites are good markers of the explosively erupted volcanic ash and can be used as stratigraphic markers on both local and regional scales. This presentation demonstrates an application of clay minerals in bentonites as indicators of diagenetic regime, particularly the paleotemperature, of pyroclastic deposits.

The mineral composition of the bentonites was analysed using X-ray diffraction and thermal analysis. The %S in the I/S packets was measured using ŠRODOŇ's (1984) technique. Paleotemperatures were calculated based on ŠUCHA et al. (1993) diagram. Zircon in heavy mineral fraction was studied by optical microscopy.

The studied bentonite beds have been identified in the Bardo Mts. – a structural unit within the Sudetes, at the northern margin of the Bohemian Massif. The structural complex of the Bardo Mts. consists of sedimentary rocks of the Late Ordovician to the earliest Late Carboniferous age. The bentonite layers occur within the Upper Viséan series composed of mudstone and claystone shales, greywackes and carbonate rocks. The bentonite beds paleontologically are “dump” (HAYDUKIEWICZ & MUSZER, 2002). Six bentonitic layers occur in the lower part of a section represented dominantly by mudstone and claystone shales. They are from 2–10 cm thick and generally light yellow to grey–brown in colour on fresh surfaces (AUGUST et al., 2003).

Examination of the bentonites shows that the major clay minerals are kaolinite and I/S mixed-layer packets. Both minerals occur in similar proportion. Chlorite, smectite and illite have been also detected in two bentonite beds. All the analysed samples contain small amounts of FeOOH substance. No relics of primary minerals were observed. Secondary calcite (up to 10% by volume) occurs in two

positions. The first one is represented by lens-like small aggregates or thin veins (0.4 cm thick) composed of fibrous crystals. The second one is represented by small crystals dispersed in the rock groundmass.

The measurements of %S (20–30%, R1–R3) in the I/S packets in the Lower Carboniferous bentonites from the Bardo Mts. testify that the maximum diagenetic paleotemperatures in these rocks attained ca. 120–135°C. The heavy mineral fraction of the bentonites contains idiomorphic zircon crystals, which clearly show their pyroclastic origin. The mineral composition (clay minerals, calcite) of the bentonites from the Bardo Mts. point to an intermediate composition of the pyroclastic material and its parent magma. Their volcanic source was possibly located in Intra-Sudetic depression, a neighbouring structural unit, where the presence of Lower Carboniferous andesites and rhyodacites was documented (AWDANKIEWICZ, 1999).

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Development of a simple method for Ar/Ar dating of micrometer-sized minerals: a progress report

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Dating of micrometer-sized minerals, first of all illite and interstratified illite/smectite (I/S) have a unique importance in geochronological studies of a set of rock-types and of geological processes. E.g. (i) in sinking basins illite formed by diagenesis can be dated. (ii) The age of illite–muscovite from low- and very low-grade metamorphic rocks will give the time of metamorphism. This method is efficient, when it is connected with “crystallinity” measurement of phyllosilicates (ÁRKAI et al., 1996). (iii) Time of tectonic activity can be confined when illite from shear-zones is dated (ÁRKAI et al., 2000, 2002). (iv) Fine-grained minerals can be used for dating (ore-)mineralization processes.

Recently conventional K/Ar dating is replaced in many laboratories by the more advanced ⁴⁰Ar/³⁹Ar (shortly: Ar/Ar) method. This method has numerous advantages: e.g. ages are more accurate and smaller amount of mineral is needed for a measurement. Among the few drawbacks the most serious is its unsuitability for dating micrometer-sized minerals. Namely, during irradiation in the nuclear reactor, in the ³⁹K(n,p)³⁹Ar reaction the ³⁹Ar nuclei are recoiled with energies in the 0–400 keV energy range. A part of energetic ³⁹Ar atoms formed near to the surface may leave the mineral and a depleted layer of 0.08 μm will be formed (TURNER & CADOGAN, 1974). The partial escape of ³⁹Ar will result in erroneously old ages.

Efforts to solve the task of Ar/Ar dating of illite and I/S have been stimulated by the chronological importance of these minerals. A reliable but very sophisticated method has been published by ONSTOTT et al. (1997). They sealed the mineral before irradiation in a quartz ampoule from which the ³⁹Ar leaving the mineral could not escape. Before degassing the mineral, regarding the high melting point of quartz, the ampoule must have been broken in the extraction line. The high melting point of quartz and the need to break the ampoule in vacuo made the experimental work very complicated. Due to these difficulties, in spite of its geochronological importance, the potential benefits of dating illite and I/S are only partly exploited.

The purpose of the present work has been the elaboration of a simple, routinely applicable experimental method for Ar/Ar dating of micrometer-sized minerals.

Our first idea was mixing the mineral with a low melting point salt and fuse them together in vacuo. It has been expected that recoiled ³⁹Ar will be captured in the salt. This idea was unsuccessful, due to the chemical reactions between the salt and mineral. It has been more promising when the mineral was dried in water-glass, in vacuo. However during the time from irradiation to gas extraction the water-glass absorbed water and atmospheric Ar, therefore this procedure requires storing the irradiated sample in vacuo.

Closing the mineral in Al before irradiation proved to be the solution. Minerals were placed in Al test-tubes of 99.99% purity, connected to a vacuum system with plastic tube, evacuated and pinched off the vacuum system. The essence of the process is vacuum-tight pinching off the Al test-tube. This has been realized by finding the proper quality of Al and the suitable profile of the nippers used for pinching off the test-tube.

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Clay minerals assemblage in the Upper Albian carbonate succession (Tinjanska Draga, Istria, Croatia)

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Introduction

Several clay-containing layers within the Upper Albian carbonate sequence (BARUDŽIJA et al., 2004) from Tinjanska Draga area in Istria (Croatia) were analyzed. The aim of the study was to connect their mineral assemblage with the contemporaneous diagenetic silicification of carbonates appearing in the same sequence (BARUDŽIJA, 2003; DURN et al., 2003). Therefore, 12 samples from the four different horizons were analyzed by X-ray powder diffraction (XRD). Results were compared with petrographic analysis of heavy and light mineral assemblage from the same samples.

Methodology and results

Bulk samples were analyzed by XRD. Samples were treated with NaAc/HAc and diffraction patterns of obtained air dried and differently treated (with glycerine; with ethylene glycol; 2 hours heated at 600°C; dissolved for 24 hours in hot 18% HCl) insoluble residues were also recorded. Clay fractions (<2 µm) from insoluble residues were taken and diffraction patterns of non-oriented and oriented samples were made. In order to determine clay minerals, samples were saturated with Mg²⁺ (oriented air dried samples, ethylene glycol treated samples and samples heated at 300°C/2h and 550°C/2h were prepared) and K⁺ (oriented air dried samples, ethylene glycol and DMSO treated samples, 2 hours heated samples at 300°C and 550°C were prepared) and diffraction patterns were taken.

Samples have significant percentage of carbonates (35–95 wt.% of calcite in 10 samples, and 2 samples with almost 95 wt.% of dolomite and less than 5 wt.% of calcite). Insoluble residues contain from 10 wt.% to 90 wt.% of quartz, as well as up to 5 wt. % of feldspars and variable content of phyllosilicates mainly present in clay fraction. Depending of sample, clay fractions mostly contain illite and/or mixed-layer illite–smectite dominated by illite layers, illite–smectites with higher amount of smectite layers than previous and randomly interstratified minerals. Some

other phyllosilicates, probably smectites, kaolinite and chlorites, are also present. In the total heavy mineral sample there are transparent grains (up to 50% – predominately epidote–zoisite–clinozoisite minerals, followed by pyroxenes [Cpx+Opx], garnets, hornblende and feroactinolite and some zircons, tourmalines and glaucophanes), muscovite (up to 40%), chlorite (up to 10%) and opaque minerals and grains with limonitic cover as well. In the light mineral assemblage quartz and feldspar (plagioclase) grains are the dominant components.

Discussion

Clay minerals assemblage in the Upper Albian carbonate succession from Tinjanska Draga is closely connected with silicification developed within limestones and dolomites from that section. Determined mixture of illite and highly illite–smectite clays indicate diagenesis of clays within marine conditions. Mineral association present within heavy and light mineral fraction shows a significant composition and can indicate volcanic origin of source material for development of determined clay minerals assemblage and source of silica for silicification as well.

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Upper Cretaceous–Lower Tertiary clay mineral successions of southern Haymana region (Ankara, Turkey)

Emel BAYHAN

Study area is located south of Haymana, near the town of Ankara. The study area consists of Paleozoic, Mesozoic and Cenozoic series and continuous marine sedimentation was observed between Upper Cretaceous and Lower Tertiary. Stratigraphical sections were measured in the study area and samples were collected along these sections. Clay minerals of the samples were determined by using X-ray diffractometry and chemical analyses of clay fraction were done using geochemical methods.

Smectite, corrensite, 14_s-14_c , illite, chlorite and vermiculite were determined in the clay fraction. Smectite is the dominant clay mineral in the Upper Cretaceous and Middle Eocene series. Corrensite and 14_s-14_c were found in large amounts in the Paleocene and Lower Eocene formations. Illite and chlorite were determined in small quantities

along the sequence. However, the illite amount increases in the Paleocene and Lower Eocene sediments. These data indicated that detrital input was important during that period. According to major elements chemical analyses smectites are determined as beidellite and saponite. Clay fraction of samples is rich in $Al_2O_3-Fe_2O_3$ or $MgO-Fe_2O_3$. Chemical analyses results show that sediments were transported from different sources. Illites and chlorites were detrital clay minerals and metamorphic rocks are the source for illites and chlorites. Smectites and interstratified clay minerals occurred from the transformation of detrital material which derived from different rocks.

Clay mineral chemistry and petrographical studies indicate that ultramafic rocks and Kırşehir metamorphic massive are the sources of clays in this area.

Clay mineralogy of Tertiary sedimentary sequence from Gökçeada Island (northeast Aegean Sea, Turkey)

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Gökçeada Island is located at Northeastern Aegean Sea, west of the Çanakkale Strait and Gallipoli Peninsula (Turkey). Study area covers Yenibademli village and its surroundings which is located at the northeast of Gökçeada Island. In this region many archeological studies have been carried out, but no detailed mineralogical studies were presented yet. This study aims to determine the whole rock and clay mineralogy of the region.

All of the rock formations in the study area are of Tertiary age. These Tertiary sedimentary units lie unconformably over the Paleozoic basement rocks. Eocene Tepeköy formation which is composed of blue-gray marls and siltstones overlies the Paleozoic units. Oligocene Kaleköy formation, consisting of light brown sandstones-siltstones alternation, succeeds the Tepeköy formation. Bademli formation conformably overlies the Kaleköy formation and consists of brown-green marl and yellow sandstones. Kuzulimanı formation unconformably overlies the Bademli formation. At the top of Oligocene sequence volcanic rocks were observed.

Samples were collected systematically along measured sections of these formations. Whole rock and clay miner-

als were determined by X-ray diffraction. The whole rock mineralogy is characterized by clay, mica, kaolinite, quartz, feldspar, calcite and trace amounts of dolomite. In the clay fraction smectite, illite and kaolinite comprise the dominant minerals. In addition to these minerals, trace amounts of 14_s-14_c were also found in the clay fraction. In general, important mineralogical differences are not observed along the Tertiary sequence. However, in the upper part of the Oligocene sequence the content of smectite decreases, while illite becomes more abundant. These differences suggest greater amounts of detritus transportation in the upper parts of the Oligocene sequence that includes sediments derived from different sources.

Petrographical studies indicated that feldspars were altered into clay minerals. It seems that great majority of clay minerals in the whole sequence occur as alteration products of either feldspars or volcanic rocks. Illites, appear to be detrital and they derived from the basement rocks. It is concluded that these sediments have been transported from various source areas, while the clay minerals derived from the basement rocks on the island and from Biga Peninsula, located on the northwestern corner of Asia Minor.

K–Ar dating of Cretaceous metamorphism recorded in the eastern part of Mt. Papuk, Slavonia, Croatia

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The Papuk is a mountain in Slavonia, the northeastern region of Croatia, situated 200 km east from Zagreb located on the very edge of Požega Valley. Three metamorphic complexes, characterized with several phases of deformation and metamorphism, can be distinguished in the Slavonia region: Psunj (Kutjevo), Papuk (Jankovac) and Radlovac (JAMIČIĆ, 1983). The research is based on studies concerning the Radlovac metamorphic complex and the Kutjevo transect (including sedimentary rocks and Psunj metamorphic complex). Analyzed samples comprise different varieties of rocks of the different petrological characteristics and age (Table 1) which range from the Late Precambrian to the Early Triassic (JAMIČIĆ & BRKIĆ, 1987; JAMIČIĆ et al., 1987).

K–Ar dating was performed on whole rocks and fraction <2 μm. Concentration of potassium was determined by flame photometry and the amount of radiogenic ⁴⁰Ar was measured by isotope dilution. All samples were also studied with X-ray powder diffraction method (XRPD) to determine the mineral composition.

The whole rock XRPD analysis on samples from the Radlovac metamorphic complex (R) and Kutjevo transect (K) yields quartz, illite–muscovite and chlorite in all samples, with K-feldspar in all “K” samples and plagioclase in all “R” samples. Hematite was found in sample K8, chloritoid in samples K4 and K7 and pyrophyllite in sample K4.

According to the measured K–Ar data (Table 1), Cretaceous metamorphic (thermal) event(s) around 85 Ma (Figure 1), can be established. This metamorphism was recorded within the fraction <2 μm i.e. “illite fraction”, so these ages represent the time of dehydration of smectite and fixation of K⁺ cation in the crystal lattice of illite. The

older whole rock ages can be explained by the well known fact that parametamorphic rock types frequently contain older, detrital components.

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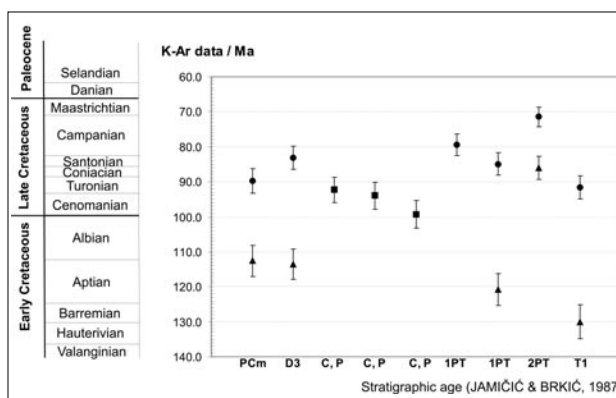


Fig. 1 Plot of K–Ar data (Ma) (whole rock and <2 μm) vs. stratigraphic age (JAMIČIĆ & BRKIĆ, 1987) for samples from Radlovac (<2 μm) ■, Kutjevo transect (<2 μm) ●, and Kutjevo transect (whole rock) ▲.

Sample	Rock type (macroscopic determination)	Stratigraphic age (JAMIČIĆ & BRKIĆ, 1987)	Measured age K–Ar (Ma)	
			Whole rock	Fraction <2 μm
K 7	Chlorite schist	PCm	112.6 ± 4.4	89.7 ± 3.5
K 4	Chloritoid schist	D ₃	113.6 ± 4.3	83.1 ± 3.3
R 4	Metasandstone	C,P	–	92.3 ± 3.6
R 1B	Metasandstone	C,P	–	94.0 ± 3.8
R 9	Phyllite	C,P	–	99.3 ± 3.9
K 8B	Metaconglomerate	¹ PT	–	79.4 ± 3.1
K 8A	Metaconglomerate	¹ PT	120.8 ± 4.6	85.0 ± 3.2
K 12	Quartz metasandstone	² PT	86.0 ± 3.3	71.4 ± 2.8
K 11	Sandstone	T ₁	130.0 ± 4.9	91.6 ± 3.3

Table 1 General information about investigated samples with measured K–Ar data of whole rock and fraction <2 μm.

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A multispectral study of clay minerals: Mössbauer, reflectance, transmittance, and emission spectroscopy

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A collection of phyllosilicates are under study using a large number of spectroscopic techniques in order to coordinate the spectral features among these different techniques with each other and the mineral structures. Our collection includes examples of chlorites, kaolin-serpentines, micas, and smectites. We are measuring Mössbauer and visible/near-infrared (VNIR) spectra in order to characterize the Fe bonds in these samples. Mid-IR transmittance, reflectance and emission spectra are used for measuring the fundamental vibrations due to Si (&other)-O tetrahedral bonds, Fe (&other)-O octahedral bonds, structural O-H and interlayer/adsorbed H-O-H. The VNIR reflectance spectra also exhibit absorptions due to overtones and combinations of the fundamental IR absorptions. The samples in the study include allophane, celadonite, chamosite, chrysocolla, chrysotile, clinocllore, ferruginous smectite, gyrolite, halloysite, kaolinite, lizardite, montmorillonite, nontronite, phlogopite, picrolite, saponite, and talc.

VNIR spectra collected by OMEGA have shown the presence of clays on Mars (POULET et al., 2005). We initiated the current study in order to prepare an archive of clay mineral spectra for the CRISM VNIR spectrometer (MURCHIE et al., 2006) that is en route to Mars, for the thermal emission spectrometer that is in orbit at Mars (CHRISTENSEN et al., 2001) and for the Mössbauer spectrometers that are currently on the Martian surface (KLINGELHÖFER et al., 2004). Identifying clay minerals on Mars provides information about the extent and duration of aqueous processes there. The VNIR and Mössbauer spectra of Mars may enable the best opportunities for identification of clay minerals because of the nature of the spectral features and the sample sizes measured on Mars.

VNIR spectra of a few samples are shown as an example in Fig. 1 in order to illustrate the variety of spectra observed for the samples in our study. The Fe bands in the 0.3 to 1.2 μm region of these spectra are being correlated with the Mössbauer spectra of these samples. The OH and H₂O bands near 1.4, 1.9 and 2.1–2.5 μm are overtones and combinations of fundamental vibrations at longer wavelengths. We are integrating the band centers of these overtones and combination bands with the mid-IR fundamental absorptions measured in the reflectance, transmittance and emission spectra as in a previous study (BISHOP et al., 2002). The Martian surface measured in the Meridiani and

Gusev regions contains a combination of ferrous and ferric minerals (e.g. KLINGELHÖFER et al., 2004; MORRIS et al., 2006). We hope through our study to be able to better characterize any clay mineral components that might be present in the Martian Mössbauer spectra.

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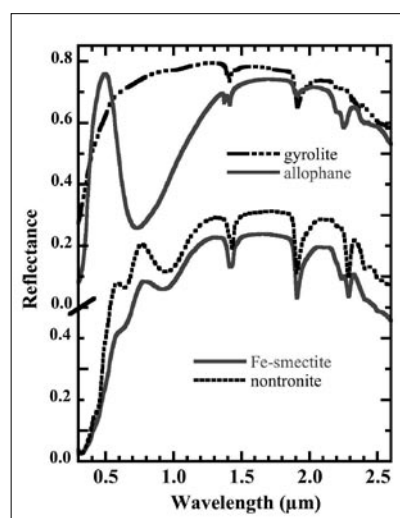


Fig. 1 VNIR spectra of a few samples.

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Production of synthetic lightweight aggregates (LWA) from mining wastes

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Mining of natural aggregates produces large volumes of waste materials in the Madrid region, central Spain (BLANCO GARCÍA et al., 2005). The problem of waste generation by quarrying fluvial aggregates is especially important along the Jarama, Tajo, Henares and Alberche fluvial systems, in view of the huge volume of fine-grained wastes. These sludges are accumulated in tailing ponds or filling voids left by the extraction process.

This work is part of a major study on the ceramic applications of wastes generated from aggregate quarries. On the basis of their mineralogy and grain-size distributions we have selected seven samples out of a total of 142 from 37 different quarries. The heterogeneity of the bedrocks eroded by the different rivers causes a significant variation in the mineralogical and chemical compositions of the wastes produced by washing sand and gravel deposits. Calcite in the wastes from the Tajo and Henares rivers may reach values of up to 55% and 45%, respectively, while it is absent in the Alberche and north Jarama river systems. The particle size distributions allow to classify the wastes as silty-clays and minor clayey silts, but sand-size particles may reach occasionally more than 15%. The clay fraction is smectite-rich in the wastes from Jarama, Henares and Tajo, and kaolinite-rich in the Alberche wastes. The silt fraction usually has higher illite contents.

The production of synthetic lightweight aggregates (LWA) has been carried out using mining wastes as unique components of the batches. The compositions were pelletized with water in a rotary disc, both with and without the use of a low volume of organic expansive agents. Four thermal cycles were designed considering the maximum temperature (1150–1200°C), heating rate (20–60°C·min⁻¹) and dwelling time (10 min). Additionally, two clay samples (ARL1 and ARL2) currently used to produce LWA in the Madrid region have been tested in parallel for comparison purposes.

Wastes from south-Jarama, Henares and Tajo rivers do not expand significantly even at 1200°C, and initial melting

is observed at higher temperatures, due to the fluxing effect of the CaO released during the thermal decomposition of carbonates. The control of the firing process became more difficult under these conditions, and a fast destabilization is achieved by using carbonate rich wastes. The Alberche and north-Jarama river wastes show higher expansion indices at lower temperatures, increasing the process of density reduction above 1200°C, and maintaining the integrity of the fired spheres. These wastes show an auto-expansive behaviour, because they can reach low densities without expansive additives. The production of aggregates with density below 1 g·cm⁻³ is possible by adding a low volume of organic expansive agent to the Alberche and north-Jarama river wastes, which show the best characteristics as LWA raw materials. The study of these compositions according to the Spanish standards (UNE-EN 1097-6/AC, UNE-EN 1097-3, UNE-EN 1744-1, UNE-EN 1744-3), and their comparison with the reference industrial samples ARL1 and ARL2, show that clayey wastes from Alberche and north-Jarama rivers can be used in the production of high quality synthetic lightweight aggregates.

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Physical properties and behaviour during leaching of synthetic aggregates made with polluted dredged sediments from Flanders, Belgium

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Dredging is a necessary tool in removing contaminated sediments from rivers, harbors, estuaries, etc. Annually, more than 9.000,000 m³ of sediments are dredged from waterways in Flanders, north Belgium (OVAM, 2003), and only about 6–7% of these underwater materials are considered as non contaminated (DE COOMAN et al., 2004). In the past, dredged sediments have been disposed along the shores of the waterways without precautions for contaminants eventually present. As a result, many areas containing elevated metal contents in relation to historical sediment disposal have been identified along waterways in Flanders (CAPPUYNS & SWENNEN, 2005). Nowadays, sediments dredged from inland waterways are mostly being land disposed in confined facilities, reducing progressively the available disposal capacity. Thus, the use of polluted dredged sediments as building materials is two fold: first, preserving the disposal capacity for a longer period, and second, transforming waste materials in useful resources.

This work deals with four polluted sediments (Zn: 600–1380 mg·kg⁻¹; Cu: 65–152 mg·kg⁻¹; Pb: 97–276 mg·kg⁻¹; Cd: 3–21 mg·kg⁻¹), dredged in the Flanders waterways, that have been studied at laboratory scale as raw materials in the production of synthetic aggregates. The sediments were tested as unique components of the batches and in mixtures (1:1) with clay (BC) traditionally used in the production of lightweight aggregates (LWA) in Flanders. These compositions were pelletized with water in a rotary disc, both with and without the use of a low volume of organic and inorganic expansive agents. Five thermal cycles were designed considering the maximum temperature (1150–1200–1225°C), heating rate (20–60°C·min⁻¹) and dwelling time (10 min). Additionally, three BC samples were tested in parallel for comparison purposes.

The high water absorption and bulk density of fired aggregates, made exclusively of dredged sediments, show the inefficiency to trap the gases generated during the thermal process, whatever the expansive agent. The porosity reduc-

tion of the external layer on these spheres increases as the maximum firing temperature increases, but is high enough to avoid the expansion process, even at 1225°C. The addition of the clay-rich component (BC) improves the density of the synthetic aggregates in all the wastes, due to a decrease in the sintering temperature, lowering the gas release. A dense glassy layer covers these samples, and a better density reduction is attained by adding inorganic expansive agents. Slow thermal cycles (20°C·min⁻¹) get higher densities in all the tested compositions, and good LWA are obtained at 1225°C, with fast thermal cycles. Leaching tests (EN 1744–3) show a low mobility of Zn, Cu, and Pb after firing. The tests now being carried out on size-reduced aggregates (EN 12457–3, NEN 7371) will assist with prediction to the long term release of heavy metals.

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Maastrichtian calcisols from the Hateg basin, South Carpathians: mineralogical and stable isotopic investigations

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Within the Hațeg basin (SW South Carpathians) the late Cretaceous was divided by STILLA (1985) into sedimentary groups, separated by local unconformities. At Tustea quarry, situated at the northern border of the basin, the 10 m vertical escarpment comprises two levels of massive red mudstones intercalated with conglomerates and cross-stratified sandstones. The bottom of the sequence is represented by a massive red mudstone followed by 4 m coarse grained, poorly sorted deposits with trough-cross to parallel stratification. The channel bodies show laterally crosscutting and alternating sandstones and conglomerates, which indicate unstable channelized flow with discharge fluctuations. The inter-channel areas, starved of coarse sediment supply, were site of pedogenesis. The soils show a red mud horizon with blocky structure characterised by the presence of well developed vertical roots and burrows and a level with calcareous concretions. There are several levels of calcretes with thickness and lateral continuity indicating moderately developed soils (RETALLACK, 2001). Paleosols can be classified as calcisols (MACK & JAMES, 1994). Associate with some of concretion layer, just above them, dinosaurs nesting sites together with embryonic/hatchling skeletal remains were found. Based on these remains, the eggs are thought to belong to a hadrosaurid *Telmatosaurus transsylvanicus* (GRIGORESCU et al., 1994).

X-ray analyses show that all paleosol samples have a bulk mineralogy dominated by layer silicates. In the <2 μm fraction, smectite, dominates with up to 94 wt.%. Other clay minerals present in very small amounts are: illite (4–10 wt.%), and kaolinite (2–4 wt.%). The positions of the OH bands in the IR spectra indicate that the smectite is montmorillonite. The <0.2 μm fraction from different paleosol levels were separated in order to make additional chemical analyses and determine the isotopic composition of the smectites. For isotopic composition measurements absorption and interlayer water were removed by heating the samples at 200°C for ~24 hours. Preliminary heating tests were done on STx-1 a CMS smectite standard. The samples were heated for 2, 4, 12 and 24 hours at 200°C and after each heating step IR spectrum was measured. Only after 24 hours heating practically all interlayer water is removed. Stable isotope measurements on oxygen were performed using a classic silicate line with Nickel bombs. The samples were firstly heated under vacuum 1 day at 200°C and than fluorinated with BrF₅ at 550°C for ~ 1 day. The δ¹⁸O com-

positions are around 19‰ (SMOW). For the hydrogen isotopic measurements the samples were also heated under vacuum one day at 200°C, and than measured on a TC/EA device in continuous flow. The δD values vary from 143 to 166‰ (SMOW). Also for the Hateg basin, measurements on the isotopic composition of the rain water have been started in August 2005.

At Tuștea, the red colour and the presence of calcretes with micritic texture indicate that the soils formed above the water table under oxidizing, alkaline conditions. The deeply penetrating vertical root traces also suggest well drained soils. These conditions were favourable for the preservation of egg and bone material. The thickness and distribution of the calcrete levels indicate multiple buried, moderate to strong developed soils, most probably developed on a stable terrace, close to the basin border. The coarse sequence is interpreted as deposited in a feeder zone of an alluvial fan during flooding events. The high content in smectite, up to 98 wt.%, was favored by the presence of the volcanoclastic material present at this site. Using appropriate fractionation factors, the isotopic data indicate that the smectites are in equilibrium with the local present meteoric water line. Equilibrium between smectite and present meteoric rain water was also put in evidence by early workers (SAVIN & EPSTEIN, 1970, LAWRENCE & TAYLOR, 1971).

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Solid-state NMR study of stability of “geopolymers” prepared from alkaline activated metakaoline

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Geopolymers defined as amorphous aluminum-silicates originate by the reaction of metakaoline with sodium or potassium water glass. During the reaction the geopolymer gel is formed, which “structure” is partially reminiscent to zeolite one. Current trends in geopolymer chemistry are to develop geopolymers systems without adding water glass. The absence of water glass makes fabrication of geopolymers significantly cheaper. The aim of our work was to examine the structure of such prepared materials and their subsequent transformations at laboratory and hydrothermal conditions.

Contrary to generation of “right geopolymers”, the first step of our preparation was calcination of metakaoline together with the mixture of NaOH and KOH. Surprisingly the structure of the resulting products is quite comparable with standard geopolymers as was nicely confirmed by solid-state ²⁷Al and ²⁹Si MAS NMR. Hydrothermal treatment and similar experiments are important for the understanding of long-term stability of metastable substations.

All the samples during treatment were subjected to measurement of the compressive strengths, X-ray powder diffraction and analysis ²⁹Si and ²⁷Al MAS NMR.

At first ²⁷Al and ²⁹Si MAS NMR experiments confirmed that structure of metakaoline was significantly altered only by calcinations with hydroxides at ca. 550°C. Subsequently

it was found out that ²⁷Al MAS NMR spectra are fairly insensitive to long-term hydrothermal treatment (only conversion of residual octahedral sites to tetrahedral ones was recognised), while ²⁹Si MAS NMR spectra provide significantly deeper insight to changes occurring at atomic level. For our inorganic systems broad ²⁹Si MAS NMR signals indicates wide range of Si environments among them Q⁴ (3Al) units predominate. As a consequence hydrothermal treatment we observed changes in ²⁹Si MAS NMR spectra which correspond to formation of structure units reflecting increase in Si/Al ratio. Up to some level of this ratio mechanical strength increase, then steep decrease was observed. NMR spectra also clearly revealed that during the hydrothermal period the second generation of “geopolymer” was formed. This period is characterized by the dissolution of the quartz and the phillipsite with the participation of the amorphous phase. The presence of phillipsite was detected in the hydrothermally altered composites whereas zeolite X (FAU) was found in the composites spontaneously aging as follow X-ray powder diffraction.

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Clay mineral template-controlled formation of molecular assemblies of rhodamine 6G

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Hybrid nanocomposite materials, which contain molecules of organic dyes incorporated in an inorganic solid matrix, are potential candidates for various applications, such as optical sensors and devices, solid lasers and in memory media. The interactions of rhodamine dyes with various inorganic solid compounds have been studied and published in numerous papers. The results of presented work confirm importance of parameters of a clay mineral template for optical properties of adsorbed cations of organic dye, rhodamine 6G (R6G).

A series of reduced-charge montmorillonites with a systematically modified charge was prepared from Nanocor montmorillonite using the standard method of Li⁺ cation fixation. Two types of hybrid R6G/clay mineral materials were studied: dispersions (BUJDÁK et al., 2004) and oriented thin films (BUJDÁK et al., 2003). The effect of the layer charge of a montmorillonite substrate on the optical properties of the adsorbed cationic dye, rhodamine 6G, was tested. The charge controlled the dye cation distribution and the formation of the dye's molecular assemblies, such as H- and J-aggregates and H-dimers. The large-order H-aggregates were formed on surfaces of clay mineral specimens with high charge densities. The dye molecular assemblies were characterized by distinctly different optical properties. Ultraviolet/visible and fluorescence spectroscopies were used for the characterization of the studied systems.

The dye/silicate dispersions are dynamic systems, where complex re-organization and re-distribution of the dye assemblies take place. The reactions in R6G/clay mineral dispersions included the formation of higher-order aggregates at the surfaces of the high charge densities, or dye deaggregation reactions at the surfaces of medium or low charge densities.

Fluorescence spectroscopy revealed the luminescent properties of adsorbed dye cations, which were adsorbed in the form of monomers. Surprisingly, also the H-aggregates exhibited weak luminescent properties mainly in the reaction system with the highest charge silicate and characterized by emission at broad range of the wavelengths.

Polarized UV-Vis spectroscopy was used for the characterization of the molecular orientation of dye cations in the films. There were several species of R6G cations in the interlayer spaces of the clay mineral host, which was easily resolvable by the polarized spectra. The cations forming H-aggregates and absorbing light at low wavelengths were oriented in nearly perpendicular fashion, which was observed as a strongly positive dichroism. Adsorbed isolated dye cations were inclined at low angles with respect to the plane of the clay mineral surface. X-ray diffraction was not sensitive enough to reflect the heterogeneous arrangement of the dye cations.

In summary, the distribution of the layer charge of a clay mineral template plays a key role in the formation of dye molecular assemblies. Choice of a clay mineral template with optimal parameters can be used as a tool to achieve desired optical properties of adsorbed organic dye. Moreover, the interaction between organic dyes and clay minerals can be useful for clay mineralogists to characterize the layer charge distribution.

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Spectroscopic study of interaction of porphyrin dyes with layered silicates

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Hybrid materials lie at the interface of the organic and inorganic realms. These materials offer exceptional opportunities not only to combine the important properties from both the fields but also to create entirely new compositions with truly unique properties (YUI & TAKAGI, 2003). Generally, dye molecules tend to aggregate on the clay surface or in the interlayer spaces. The layer charge of layered silicates controls the molecular aggregation of the dyes of various structural types (BUJDÁK & KOMADEL, 1997; BUJDÁK & IYI, 2002).

The objective of this study is to investigate the interaction of four representative cationic porphyrin dyes with layered silicates (layered silicate/porphyrin systems, LSP). As layered silicate matrices, the series of reduced-charge montmorillonites was used. These were prepared from one parent material (Nanocore) by Li⁺-saturation and thermal treatment. The effect of the layer charge is investigated in detail. Molecular aggregation is expected to be suppressed due to high electrostatic repulsion forces between the dye cations. This paper studies in detail if the molecular aggregation is sufficiently suppressed regardless the properties of silicate template. The study is based on the investigations of spectral characteristics of layered silicate/porphyrine systems (LSP) using UV–VIS and fluorescence spectroscopy.

We found out that adsorption of studied porphyrin dyes leads to the significant changes of their optical properties. The changes in absorption spectra in a visible spectral region partially reflect the layer charge characteristics of layered silicate templates. The position of a main Soret band is generally shifted to lower energies, even more significant changes are observed in the spectral range of Q-bands. Judging from these data, spectral analysis indicates the formation of J-aggregates of the dye on the silicate surfaces, characterized with head-to-tail intermolecular association.

Formation of non-luminescent “pure” H-aggregates was not confirmed in any reaction systems. This fact confirms the systems based on layered silicate/porphyrin composites as perspective materials for photochemical applications.

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Metal complex exchange in natural zeolites

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Mario ŠILJEG³ and Branka VOJNOVIĆ⁴

This study investigates possibilities of application of natural zeolite from Donje Jesenje mine in the process of removal of metal ions (zinc, chromium) and their complex compounds from galvanization and dye industry wastewaters. Natural zeolites show affinity towards the metal ions and they found wide range of application for metal ions removal from water solution, what is shown in several publications (CERJAN-STEFANOVIĆ et al., 1996; VASSILIS & GROGOROPOULOU, 2003). Detailed characterization of natural zeolite includes X-ray diffraction structural analysis, differential thermal analysis, measurements of specific surface area and density. Metal species are determined by UV/VIS and AAS.

The influence of natural zeolite treatment (granulometric and chemical treatment of natural zeolite, time of equilibrium, concentration and pH value of metal ions solution, type and concentration of ligand) on the capacity and selectivity of ions removal has been investigated. It is proved that mentioned parameters had great influence on ion exchange processes between zeolite and metal ions (ROŽIĆ & CERJAN-STEFANOVIĆ, 2002). The behavior of zeolite in contact with metal ions in water solutions is a complex problem because of appearance of zinc and chromium in several ionic forms towards which zeolite has different af-

finity (PANSINI et al., 2001). The influence of ligand in metal-complex compounds on the metal ion removal can be curtail, depending on metal-ligand, metal-zeolite and ligand-zeolite bounding strength (KOPRIVANAC et al., 1997). The influence of ligand on ion exchange processes of zinc and zeolite will be investigated. Obtained results will be the basis for Paterson and Langmuir isotherm.

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Energy transfer between cations of laser dyes in dispersions of reduced charge montmorillonites

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Fluorescence resonance energy transfer (FRET) is a phenomenon of energy transmission between an energy donor and acceptor molecules. The occurrence of the energy transfer is limited by the properties of interacting components and depends on intermolecular distances and spatial molecular arrangement. FRET requires a spectral overlap between emission and excitation spectra of energy donor and acceptor components, respectively (LAKOWICZ, 1983). The energy transfer does not normally proceed in dilute solutions due to large intermolecular distances, but may occur after the concentration of interacting molecules at interfaces. Smectites represent appropriate templates to be used to concentrate cationic dyes on their surfaces. Moreover, the layer charge of smectites sensitively controls the cation distribution of dyes and formation of various types of supramolecular assemblies (BUJDÁK, 2006), which may be significant for the processes of FRET.

The objective of our work was to study the energy transfer between two cationic laser dyes, rhodamine 3B (R3B) and oxazine 4 (Ox4), in dispersions of reduced charge montmorillonites (RCMs). The series of RCMs were prepared using a standard method of Li⁺-fixation (KOMADEL et al., 2005) in Nanocore montmorillonite at 100–300°C. The charge reduction was expressed as the decrease of values of cation exchange capacity (CEC). The CEC, as well as the layer charge gradually decreased with increasing temperature of RCMs' preparation. Li⁺-fixation led in some cases (treatment at >130°C) to the loss of material expandability due to the formation of non-swelling interlayer spaces.

The FRET was investigated by means of fluorescence spectroscopy. The efficiency of FRET in studied system was found to be very sensitive to the layer charge and swelling of smectite. Dye species, which were formed on montmorillonite surface, included isolated dye cations and molecular assemblies, such as H- and J-aggregates. The molecular assemblies were identified using ultraviolet/visible spectroscopy. H-aggregates, characterized with a sandwich-type intermolecular association, are non-fluorescent. Moreover, they significantly quench luminescence of other species and reduce FRET yields. On the other hand, J-aggregates of a head-to-tail intermolecular association are luminescent. Fluorescence spectroscopy confirmed absence of energy transfer from R3B to Ox4 in dispersions with

parent Li⁺-montmorillonite. High charge density on the surface of clay mineral induced formation of H-aggregates which quenched luminescence. The FRET was detected for the reaction systems with lower charge montmorillonite templates, prepared by Li⁺-fixation at 100, 110 and 120°C. The FRET was accompanied with a significant reduction of the luminescence from energy donor, R3B cations, which initially received the energy from electromagnetic radiation and played the role of light harvesting antennas in this system. After excitation of R3B cations, the energy was transferred to neighbouring Ox4 cations (energy acceptors), which was followed by significantly enhanced fluorescence from Ox4 cations. Reduction and increase of the luminescence from R3B and Ox4, respectively, indicated the efficiency of an energy transfer process. The efficiency was closely related to the layer charge and increased with the charge reduction achieving optimal values for the system with a clay mineral template prepared by Li⁺-fixation at 120°C. Further decrease of the layer charge resulted in lowering of the energy transfer efficiency. This could be interpreted in terms of increasing intermolecular distances between cations representing the energy donors and acceptors. A substantial reduction of the charge (samples prepared at 140–300°C) led to absence of the FRET. Probably, the adsorption sites for these cases were so far apart, that large intermolecular distances did not allow the resonance between R3B and Ox4 molecules. Furthermore, lower expandability of clay minerals might have led to entrapment of a part of dye molecules isolating them from potential neighbours, thus reducing the yields of FRET.

In summary, clay minerals can act as templates in energy transfer processes. The significant result of this work is that the parameters of clay mineral templates, such as layer charge density and distribution or material expandability, play a crucial role for the overall efficiency of the process.

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A new approach to the interpretation of Fe²⁺ quadrupole doublets in Mössbauer spectra of dioctahedral *trans*-vacant micaceous minerals

Lidia G. DAINYAK

Crystal-chemical and structural peculiarities of 2:1 dioctahedral *trans*-vacant Fe-rich phyllosilicates provide the unique possibility to refine their Mössbauer spectra using models which account for the sensitivity of the spectroscopic methods to the short-range order in cation distribution. We began developing such models more than two decades ago (DAINYAK et al., 2004, and references therein). The principal idea of our approach is that the main factor responsible for the variety of EFGs affecting Fe nuclei is their local cation environments in octahedral sheets. Therefore, the fitted quadrupole doublets with their splittings, Δ_j , the number of which is limited by spectral resolution, can be presented as superpositions of individual quadrupole doublets with a small range of quadrupole splittings, Δ_i . Each Δ_i corresponds to Fe nuclei in one of local cation arrangements (3Fe³⁺, 3Al, 2AlFe³⁺, MgAlFe²⁺, etc.) with occurrence probabilities, w_i . When the quantitative assignment of the Δ_i values to this or that local arrangement is known, the problem of determining the “fine structure” of the j doublets can be solved by simulation of two-dimensional cation distribution (CD) characterized by certain w_i values for various local arrangements around Fe³⁺ and Fe²⁺. Then the CD reconstruction satisfying both the areas under the doublet components, S_j , and Δ_j values is regarded both as the spectrum interpretation and the peculiarity of the mineral under study.

The assignment of the Δ_i values for Fe³⁺ was reported by DRITS et al. (1997). It is provided by the empirical equation including the dependence of Δ_i^{pred} on charge and size heterogeneity of the local Fe³⁺ environment. The reliability of the Δ_i^{pred} values is confirmed by the fact that the CDs simulated according to these values for celadonites, glauconites and ferriillites satisfy experimental data obtained

by EXAFS and IR spectroscopies and chemical analysis (DRITS et al., 1997).

Combination of the Δ_i^{pred} values for Fe³⁺ doublets with the new version of the program for two-dimensional CD reconstruction provides, for the first time, the interpretation of Fe²⁺ quadrupole doublets in terms of the local structure. The resulting CDs for a representative collection of *trans*-vacant dioctahedral celadonites, glauconites, ferriillites and leucophyllites display correlations between Δ_j of Fe²⁺ fitted to the corresponding spectra and cation composition of local cation arrangements around Fe²⁺ with their occurrence probabilities. Based on these correlations, the individual Δ_i^{tent} for Fe²⁺ referred as “tentative” have been derived.

The order of local cation arrangements in terms of increasing quadrupole splitting was found to be the same both for Fe³⁺ and Fe²⁺ and implies a direct dependence of the Fe²⁺ quadrupole splitting on the structural distortion at Fe²⁺ site.

The set of Δ_i^{tent} for Fe²⁺ combined with Δ_i^{pred} for Fe³⁺ and with the new CD simulation program provide an additional means for controlling the CD reconstruction.

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Influence of controlled mechanical deformation on structural, thermal and technological properties of commercial talc

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Layer silicates used in industrial applications generally undergo a grinding process which besides refining the particle size can also induce significant changes in structural and physical properties which, in turn can affect the technological application of the material. Because during grinding various parameters (temperature, pressure, mechanical energy, etc.) can influence the structural modifications of talc, mechanical deformation was performed in controlled environmental condition. Mechanical treatment, which involves simultaneous compression and shear, was applied to commercial talc through planetary ball milling by a specifically built apparatus working in controlled thermodynamic conditions, as already successfully applied to others layer silicates (DELLISANTI & VALDRÈ, 2005). XRD, FT-IR, DTA-TG and BET analyses were performed for the characterization of the material. Commercial talc (talc content higher than 95%) was mechanically treated for 1, 5, 10 and 20 hours at room temperature in vacuum.

As a non-linear function of the treatment time a progressive reduction of structural order related to crystallite size decrease and to an increase of both lattice defects and microstrain was observed. In particular, it is to be noted that mechanical treatment causes delamination for short times (up to 1 hour), whereas a destabilization of all structure occurs for longer times. However, degradation of talc was not followed by amorphization of the mineral and also after 20 hours of treatment the talc structure was maintained. Initial stages (up to 5 hours of treatment) were also characterized by increase of specific surface favouring water absorption, whereas for longer times a re-aggregation of material by a cold welding mechanism occurred.

Infra-red data showed that deformation mostly affects the Mg-OH bonds within octahedral layer leading to a structural destabilization in the overall TOT structure, even though lesser modifications were observed in the bands relative to the Si-O-Mg and Si-O bond. The destruction of octahedra occupied by Mg could induce a variation of layer charge and charge distribution similarly to that observed for Mg-rich montmorillonites by CHRISTIDIS et al. (2005), however specific measurements were not at the moment performed.

The structural disorder induced by the mechanical treatment produced a generalized anticipation of about one hundred degrees of the maximum temperature of dehydroxylation of talc. Instead of the classical temperature of about 930°C we observed the dehydroxylation at 840°C for talc deformed for 20 hours. In addition, the dehydroxylation occurs in two stages probably due to the presence of different size and crystallinity of particles of talc or because some amounts of ineffective talc were still present. Furthermore, it was noted that the release of structural water in deformed samples starts already at temperature lower than 300°C in a continuous monotonic way as a function of treatment time. The overall loss of OH at lower temperature range progressively increases. Finally, the deformed material is more thermo-reactive in respect to the untreated one, in fact the recrystallization of talc in enstatite is anticipated at temperature of about 850°C instead of the classical recrystallization at about 1000°C.

In conclusion, we reported that mechanical deformation conducted in controlled conditions leads to a different grade of modification of structural, physical and thermal properties of talc. In particular, for short treatment times delamination along ab plane was observed, followed from maximum changes in the structure of talc after 5 hours and finally the degradation increases, but in a less relevant way, for longer treatment times. Further investigations involving particle size distribution, colour (measurements according to the CIELAB system) and rheological properties are in progress to evaluate if the different structural changes of commercial talc could be exploited in specific technological applications.

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The origin of mineral and energy resources of Central Europe (accompanied by metallogenic map 1:2.500,000)

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Central Europe looks back on more than 2000 years of mining and on more than 500 Ma of ore mineralization and deposition of non-metallic and energy resources. The area under consideration extends from eastern France to western Russia and from southern Denmark to northern Italy, it covers the boundary between the Variscan and Alpine metallo-tectonic units which host some of the most well-known deposits on earth, e.g. Rammelsberg (Germany), Kupferschiefer (Germany, Poland), Bleiberg (Austria), Jáchymov (Czech Republic), Idrija (Slovenia), Kremnica (Slovakia), Les Baux (France). Many of them have significantly contributed to the understanding of the origin of similar deposits elsewhere in the world, although many of them can today no longer be termed deposit by world standards. Excluding the base metal deposits in Poland, it is mainly coal, salt and a wide range of non-metallic commodities which render Central Europe to rank high up in the list of raw materials even by world standards.

The Variscan metallogenesis in Central Europe outside the Alps with predominantly granitophile elements is denominated as an “ensialic metallogenesis”, acting under more or less closed-system conditions, whereas the Alpine successor shows all the hallmarks of an “ensimatic metallogenesis”, when for a period of time the system was open for elements to be introduced from subcrustal sources. Part of the Variscan metallogenesis was re-activated during Alpine metallogenesis and incorporated into the Alpine metallogenesis. The Variscan metallogenesis may largely be taken as a continuum, whereas the Alpine metallogenesis in the extra-Alpine region as well as in the Tethyan basin is either

indirectly or directly affected by the formation of an oceanic crust in the Penninic, Meliata and Vardar zones.

The Variscan and Alpine metallogenetic successions are not very much different as far as the types of deposits are concerned. A sequence of stratabound, thrustbound and collision-/granite-related deposits developed during the Variscan and Alpine metallogenesis. The late Variscan/early Alpine and Subhercynian/Laramide/late Alpine uplift resulted in the formation of a set of unconformities, or in geomorphological terms, peneplains with which supergene and hypogene mineralizations are associated. The limit between the late and early Alpine epochs of unconformity-related mineralization coincides with the period of maximum spreading in the Alpine Tethys during the mid-Jurassic. Re-mobilization was triggered along deep-seated fault zones during various periods of the Variscan and Alpine metallogenetic cycles, the most far-reaching processes of this type occurred during the Cenozoic along, e.g., the Rhein Graben where a new cycle is going to start off. In Central Europe hydrocarbons were trapped all along the Meso- and Cenozoic. At the eastern edge of the Variscan craton hydrocarbon trapping has already started during the Paleozoic.

A classification of non-metallic and metallic deposits as well as energy resources has been performed for Central Europe covering an area from eastern France to western Russia and from southern Denmark to northern Italy and a time span from the late Proterozoic to the Recent. The most important deposits, excluding construction raw materials were shown on a map on the scale 1: 2.500,000.

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Mineralogical transformations during firing of some Plio–Quaternary clays from NE Slovenia

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Natural clayey raw materials differ in mineral and chemical composition as well as in granulometric distribution and therefore show different drying and firing properties that are of decisive importance for the quality of the end products (BAULUZ et al., 2003; DONDI, 1999). Mineral transformations as well as formation of liquid phase in the firing process depend on raw material characteristics and can be influenced by heating velocity and soaking time.

With the aim of studying the mineral changes occurring during firing of clays and ceramic bodies with different mineral composition and granulometry, composite samples of Plio–Quaternary clays from secondary deposit on Pannonian basin margin hills, NE Slovenia, were analyzed for their mineral and granulometric composition and fired at different temperature stages.

These clays are of illite–chlorite composition with different smectite content. They are of intermediate plasticity with high quartz content. Feldspars (both K-feldspar and plagioclase) are present in all samples, while carbonates (calcite and dolomite) occur in some samples as well. The less than 2 µm particle size fraction varies in the 35–53% range. According to particle size distribution, these raw materials belong to silty clay or clayey silt, and could be appropriate for roofing tiles and lightweight blocks and par-

tially for thin walled hollow bricks as we can predict from WINKLER (1954) diagram as well.

Samples were milled and homogenized, extruded, dried and fired at different temperatures from 800°C to 1100°C, with same soaking time and slow cooling.

Mineral composition of raw material (bulk and oriented <2 µm sample) and fired products as well as the amorphous phase content were determined by means of X-ray powder diffraction. Polished thin sections were prepared for mineralogical and textural analysis. The transformation temperatures of raw material minerals during firing and the temperature of melting were determined.

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Application of IP method for discovering clay zones in carbonate terrains

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Introduction

Induced polarisation (IP) method has been often applied in dissipated sulphide ores exploration. Besides sulphide ores, clay sediments can also show anomaly strong IP effects. This effect has been termed as a membrane polarisation, which is probably due to ionic exchanges and setting-up of diffusion potentials (PARASNIS, 1997). Because of that, there is a possibility of discovering clay zones using IP method. Method can be very interesting in hydrogeological explorations in karst terrains. In such terrains water can usually be found in faulted and fractured zones that are showing significantly lower resistivities than the compact rock. Similar decrease of resistivity can occur due to a presence of clay in fractured carbonate zones. Clays can show IP anomalies and therefore it is theoretically possible to distinguish fractured zones with water from fractured zones with clay.

Resistivity and IP measurements

Resistivity and IP measurements were carried out on two profiles. Location of the first profile was Manojlović vrelo near Ogulin, and the second profile was set out in Velika Jamnička near Zagreb. Manojlović vrelo is situated in karst terrain and Velika Jamnička in aluvial terrain.

The measurements were performed using Wenner electrode array and 10 m unit electrode spacing. The time domain IP method was used. Measured data have been expressed as apparent chargeabilities of the medium. For

each measurement three full cycles were used and the current on time was 2 s. Chargeability was measured during the first time interval, 100 to 150 ms after the current had been turned off.

Apparent chargeabilities were transformed into true chargeabilities using inverse modelling to define subsurface chargeability distribution.

Results

Manojlović vrelo profile showed low values of chargeabilities (0–5 ms), and there were no IP anomalies on this profile. In the middle part of resistivity profile there were low resistivities (200–500 Ωm) that indicated the presence of fractured zone. This fractured zone may be filled with water or with clay. However, the values of chargeability were not increased in this part of profile and therefore it was concluded that the fractured zones were filled with water. On the Velika Jamnička profile (Fig. 1) very high values of chargeability were discovered (more than 50 ms). These anomalies generally match with zones of low resistivities in resistivity profile on this location and indicate the presence of clay sediments. Measurement results on these two examples indicate that zones with water can be distinguished from clay zones using combined application of IP method and resistivity method.

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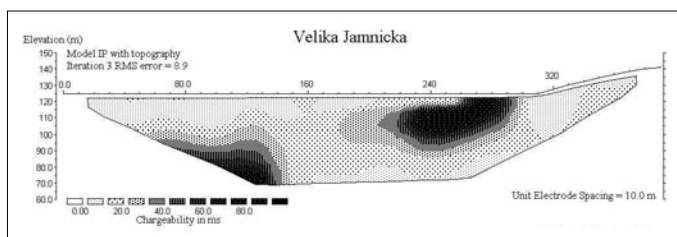


Fig. 1 Interpreted IP profile Velika Jamnička with two main anomalies indicating clay zones.

Mechanism of As sorption on Fe-treated clays

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Adsorption of arsenic from aqueous environment on clay surfaces becomes more and more important for economic reasons. Most of the considered natural aluminosilicates belong to low-cost and environmentally acceptable materials.

Two methods using Fe^{II} and Fe^{III} salts were applied to the pre-treatment of natural clay minerals to improve their sorption efficiency to As^V and As^{III} species. Different types of clays, natural kaoline from the Merkur quarry, Czech Republic, calcined at 550°C, and a raw bentonite from mineral deposit in Hajek, Czech Republic, were used. In the first process the initial material was exposed to concentrated solution of Fe^{II} (0.6 M FeSO₄·7H₂O) for 24 hours (BONNIN, 2000). In the second process the sorbents were treated with partly hydrolyzed Fe^{III} (0.025 M Fe(NO₃)₃·9H₂O; 0.05 M NaOH) overnight. The results showed that the method with Fe^{II} was more appropriate for the kaoline treatment (sorption efficiency of As^V ≈ 98/28 %; As^{III} ≈ 30/33 %), whereas for the bentonite treatment the procedure with Fe^{III} was excellent (>99% efficiency for both the As^{III} and As^V sorption).

Metakaoline was more sensitive to the type of pretreatment, therefore only Fe^{II}-treatment was usable for As^V sorption. Both methods of treatment were applicable to bentonite, while Fe^{III}-treatment was much more effective. Arsenates were better adsorbed in all systems than arsenites. The appropriate reaction time for reaching the equilibrium state was 24 hours for the sorption on the bentonite and/or 72 hours on the metakaoline.

The mechanism of Fe-treatment and subsequent sorption processes depended on the structure of raw material, method of treatment, initial solution properties (pH, As^{III}/As^V concentration) and reaction time (DOUŠOVÁ et al., 2005). It is evident, that As^V was entirely bound as arsenate

tetrahedrals to available Fe³⁺ particles (ion-exchangable or ferrihydrite) forming the stable inner-sphere surface complexes (SHERMAN & RANDALL, 2003). The adsorption of As^{III} oxyanions, ran in a different manner; in the case of all metakaoline sorbents did not change the initial valence during the sorption process and were bound in trivalent forms. The sorption of As^{III} on Fe^{II}-treated bentonite gave the same results; the Fe^{III}-treated bentonite was able to bind As only in a pentavalent form, which considered the oxidation of arsenites to arsenates during the sorption process. The final oxidation state of adsorbed arsenites was probably connected to the character of available Fe³⁺ particles on the sorbent surface, steric effect and sorption kinetics; small, single Fe³⁺ particles (resulted from Fe^{II}-treatment) appeared to be more suitable as arsenites binders keeping the trivalent state. The larger FeOOH aggregates (resulted from Fe^{III}-treatment) were attracted to more porous bentonite surface forming stable Fe^{III}-As^V inner-sphere complexes. The unoccupied active Fe³⁺ particles on the sorbent surface were transformed to more stable and/or crystalline oxidic forms.

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Micromorphology of the pedo-sedimentary colluvial complex in Sjenokoša (Istria, Croatia)

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The Sjenokoša profile represents an 850 cm thick complex situated in an uvala type of karst depression composed of an Upper Pleistocene loess complex above a colluvial complex showing superimposed features of colluviation and soil formation. An attempt to compare field observations and micromorphological research with the results of chemical analyses will be presented.

Clay bulges on the textural log nicely coincide with the soil horizons established on site by visual inspection. With the exception of the lowest part of the profile, clay illuviation is a conspicuous feature throughout the profile. The detrital fraction in the groundmass is fairly constant throughout, both from the point of view of grain size and quantity, implying a fairly constant supply of silt size detritus and fine clay. It is only the “detrital” event in the upper part of the profile, which indicates a sudden change both in quantity and in grain-size distribution of the detrital grains.

The middle and lower part of the Sjenokoša profile is a colluvial complex showing superimposed features of colluviation and soil formation. It seems as if it were an aggradational system, intermittently receiving moderate amounts of fine, probably preweathered clayey material mixed with detrital silt. Pedological features suggest a strongly seasonal, warm humid climate. It is not unlikely that part of the aggrading material was blown to the site of deposition by winds during the dry season and was trapped by the vegetation which could easily “digest” the excess dust with the

help of moisture provided in the rainy season. The amount of clay, the argillic horizons, and the voluminous clay coatings all suggest that the ecosystem which this kind of colluvial soil complex has “nurtured” must have been that of a woodland.

Both, episodic soil erosion and the sheet-wash detrital influx in the upper part of the profile may be considered as signs of developing semi-aridity, culminating in the deposition of the covering loess-complex (last glacial).

Although sampling for chemical and textural composition was not simultaneous with sampling for micromorphological studies, a quite good agreement exists between the results of the two independent studies for the middle part of the Sjenokoša profile (DURN, 1996). Namely, in that part of the profile sampling distances (and thickness of sampling intervals) were very similar. Samples in the middle part of the profile which have the lowest values for weathering indices ($\text{Na}_2\text{O}/\text{K}_2\text{O}$, $[\text{CaO}+\text{MgO}+\text{Na}_2\text{O}+\text{K}_2\text{O}/\text{Al}_2\text{O}_3]$, $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Fe}_2\text{O}_3$) were micromorphologically recognised as Bt horizons. Also, sample which has the highest values for weathering indices was recognised as a possible A–E transition horizon.

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Clay minerals in Jurassic bauxites and associated cover “blue hole” sequence (Istria, Croatia)

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The Rovinj bauxite occurs at the contact of Upper Oxfordian–Lower Kimmeridgian and Upper Tithonian strata in an apparent stratigraphic gap of a relatively short duration (about 6 MY) and is considered that of a passive plate interior under interplate stress (Type 2 sensu D'ARGENIO & MINDSZENTY, 1995). The uppermost 20 to 30 cm of the bauxite is heavily altered: its colour is greenish–grey to yellowish–white with vertical to subvertical extensions penetrating the underlying deep red bauxite. Above the altered bauxite the lowermost part of the cover records the establishment of a palustrine–lacustrine environment with greyish, organic-rich marl and brecciated limestone, characterized by a very restricted fauna and probably representing a freshwater pond, formed as the groundwater table was pushed upwards by seawater rising through karstic channels from below. Greenish–grey to yellow clay intercalations in the coverbeds may be signs of ephemeral exposure or, alternatively, represent clay influx from adjoining slightly more highly elevated areas (still exposed when the depositional environment was already inundated).

The dominant mineral phases in both red and grey bauxite are kaolinite and boehmite. The main iron bearing phase in red bauxite is haematite and in grey bauxite pyrite. Both bauxites also contain chlorite and mixed layer chlo-

rite/vermiculite/illite. The mineralogy of the iron bearing phases and chemical composition clearly indicates that red bauxites were deposited under oxidizing conditions (vadose bauxites), while grey bauxite at the top of red bauxite, formed in a reducing environment as a result of hydrological change due to deposition of the coverbeds (phreatic bauxite). Since chlorite is present in similar amounts in red and grey bauxite, its origin cannot be related solely to the reducing processes which affected the top of the red bauxite and converted it to grey bauxite, but also to burial diagenesis. The immediate cover of grey bauxite is yellow clay dominated by kaolinite, while chlorite and mixed layer chlorite/vermiculite/illite are present in similar amounts as subordinate phases, and illitic material as traces. We tentatively propose that this clay represents redeposited material introduced to the depositional environment from the kaolinitic and bauxitic blanket covering adjoining slightly higher elevated areas.

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The influence of physical alteration on the Mössbauer and reflectance spectra of antigorite and applications to soil alteration processes on Mars

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Phyllosilicates have been found in small isolated regions on Mars (POULET et al., 2005). Characterizing clay minerals and other aqueous alteration species on Mars provides key information about the extent and duration of aqueous processes there. The purpose of this study is to characterize changes in the mineral grains resulting from grinding, and to assess the influence of physical processes on clay minerals on the surface of Mars. Samples were ground for 1, 3, 10 or 30 minutes in a vibration grinder. Physical alteration through grinding affects the structure and properties of antigorite (DRIEF & NIETO, 1999) and kaolinite (REYNOLDS & BISH, 2002). This project builds on an initial study (BISHOP et al., 2003) and includes a combination of SEM, HRTEM, reflectance and Mössbauer spectroscopies. Grain size was found to decrease, as expected, with grinding. In addition, nanophase carbonate, Si-OH and iron oxide species were formed. Here we focus on the Mössbauer spectra in order to relate our study to Mössbauer spectra of Mars (KLINGELHÖFFER et al., 2004).

Mössbauer spectra are dominated by the presence of magnetite and antigorite (Fig. 1). The fits to the sextets correspond well to those published for magnetite at 293K, with the $\delta \approx 0.30$ mm/s sextet assigned to high-spin tetrahedral Fe^{3+} and the $\delta \approx 0.67$ mm/s sextet assigned to charge transfer between Fe^{2+} and Fe^{3+} on the B (octahedral) sites (MURAD & JOHNSON, 1987). Two of the paramagnetic doublets have parameters closely matching those reported for other serpentine mineral species (O'HANLEY & DYAR, 1993). The doublet with $\delta \approx 1.11$ mm/s is assigned to octahedral Fe^{2+} , and the doublet with $\delta \approx 0.27$ mm/s is tetrahedral Fe^{3+} . The remaining doublet, which is extremely small (about 3% of the total area) and is poorly constrained in terms of position, has parameters that cannot be assigned to either magnetite or antigorite; we suspected that this doublet might be an artifact or a representative of an amorphous phase. In hopes of clarifying this issue we reran all samples at lower temperatures (150 and 12K).

These low temperature spectra are very complex and a unique interpretation is difficult. However, two trends are apparent. First, the amount of Fe^{3+} in the antigorite appears to increase slightly, from 5% of the total Fe to 13%. This is a predictable result given the heat of the grinding. Second, the percentage of Fe in the sextets with high hyperfine fields changes with grinding. The sextet with $\delta \approx 0.32$ mm/s (magnetite or maghemite) decreases in area, while

the sextet with $\delta \approx 0.53$ mm/s (magnetite or hematite) increases in area with grinding. It is possible that these sextets are simply swapping area in the fits, but the consistency of the changes (and the fact that the fits are unconstrained) does seem to indicate that an actual change in the oxide phase might be occurring. Finally, the apparent "amorphous" phase in the room temperature fits does not appear in the low temperature fits. One possible interpretation of that doublet is that it might in fact be an incipient sextet that is too small to resolve properly in the 295K data.

We are integrating the changes observed in the Mössbauer spectra as a function of grinding with related changes observed in the visible-infrared reflectance spectra.

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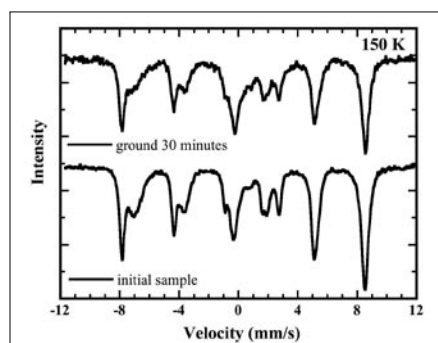


Fig. 1 Mössbauer spectra of the initial and ground samples.

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Fluidised bed technology for drying and milling of clay minerals

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A special kind of the fluidised bed process is the jet layer process. The advantage of this technology is that in single equipment a drying process and a milling process for clay minerals can take place at the same time.

The company Pilot Pflanzenöltechnologie Magdeburg e.V., in co-operation with the University of Magdeburg, developed and tested a technology for the drying and cutting up of clay minerals. After an acid activation process clay minerals can be also used as bleaching earth for the refining process of vegetable oils. In a new pilot plant of the PPM company the new jet layer technology was tested in an extensive test program. In this technical pilot plant aqueous suspensions with a solid content of up to approx. 30% were tested.

As raw material Friedländer clay/tone was used. The Friedländer clay/tone comes from Mecklenburg-Vorpommern in the north of Germany and is a mixed-layer mineral with a high part of muscovite – montmorillonite, which is interesting particularly for adsorption processes for bleaching of vegetable oils.

The attempts were evaluated especially considering the following quality indices: grain spectrum and humidity content of the final product, throughput performance, BET surfaces and especially the bleaching activity concern-

ing the adsorption of chlorophyll content of the vegetable oil. The necessary bleaching tests were accomplished in a standardized procedure with rapeseed oil.

In the technical pilot plant clay/tone minerals with a grain spectrum up to 40–140 µm were processed. The humidity content for the final product in the cyclone could be lowered with very different output products (10–80% water content) up to 2%. The throughput performances amounted 8 to 18 kg/h. Tests for the processing of chemically activated aqueous clay/tone suspensions were also successful.

The result of the trials is the development of a technology for drying and cutting up of bleaching earths and/or their base products which can take place in very simple equipment without maintained rotary parts and large mechanical mills and dryer mechanisms. As processing products both solids and suspensions can be used. The high quartz portion in the clay mineral remains without provable influence on the technology. The desired drying step and grain spectra are adjustable in certain ranges by variation of the process conditions.

Presented results, obtained on Friedländer clay/tone, can be transferred also to other products with similar characteristics.

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Mineralogical and geochemical characteristics of loess/paleosol section in Šarengrad, Srijem, Croatia

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The Pleistocene loess and Holocene alluvial sediments are dominant lithological members of Eastern Slavonia. The Upper Pleistocene loess/paleosol section “Šarengrad”, representing the oldest loess deposits in the region, was investigated using field and laboratory research methods (GALOVIĆ, 2005). Investigated section is located on the south bank of the Danube River near Šarengrad in the easternmost part of Croatia. The section was investigated on the several vertical profiles with a total length of 16.20 m.

The section is characterized by interchange of loess horizons formed during glacial (stadial) periods and paleosols developed during interglacials (interstadials). Throughout the section, four paleosol levels, represented by B- and C-horizons, are recognized. A-horizons are eroded from all paleosols. The oldest, hydromorphic paleosol is followed by laminated alluvial sediment and the loess. The second paleosol is well developed dark brown soil, about 2 m thick. The other two soils are less developed brownish paleosols.

The laboratory investigations included X-ray diffraction analysis, grain size analysis (sieving and aerometry); microscopic analyses of light and heavy mineral fraction, chemical analyses of major and trace elements, determination of carbonate content by Scheibler procedure and determination of pH and TOC.

The mineral composition was determined by X-ray diffraction using Philips diffractometer with CuK α radiation on ten randomly oriented powdered bulk samples of loess and different paleosols, as well as on their clay fraction (<2 μ m) that was separated by sedimentation. The bulk mineral composition of all samples is typical of loess/paleosol sequences. Major phases are quartz, white mica, feldspars and chlorite, as well as carbonates (calcite and dolomite). The carbonates occur in very small amounts and lack in some samples of two older paleosols. Minor phases are amphiboles. Other heavy minerals as op \hat{a} que miner-

als, chlorite, biotite, epidote–zoisite, amphibole, pyroxene, garnet, kyanite, staurolite, tourmaline, zircon, rutile, titanite, apatite and chromite are proved only by microscopic investigations. The clay fractions are composed mainly of illitic material, chlorite and smectite. Kaolinite, proved by DMSO, is present in negligible amount, and lacks in the third paleosol. Small amount of interstratified mineral with smectitic and illitic layers as well as chloritic and vermiculitic layers are also present.

The main grain size fraction is represented by silt. Higher content of clay fraction is present in paleosol horizons, especially in second, well developed soil where pedogenic process was intensive. The carbonate content is highest in BC- and C-horizons as a consequence of migration and accumulation processes. The only exception is the oldest hydromorphic paleosol. The modal analyses show strongly abraded typical aeolian spherical grains characterized by pitted well-rounded surface. Paleosol horizons could be clearly extracted based on weathering coefficients, Ba/Sr, and $(CaO+Na_2O+MgO+K_2O)/Al_2O_3$ ratio. The content of REE, as well as trace elements, are higher in paleosol than in loess horizons. Elementary statistics shows no significant difference in chemical composition between profiles. Loess horizons contain <0.1% of TOC, while paleosol horizons contain between 0.1 and 0.5% of TOC. Based on TOC values, we can distinguish the sub-groups of samples selected according to the degree of soil development. The results of F- and t-tests show that weathering coefficient Ba/Sr fits the criteria of equality of variances and means in less developed paleosols and paleosols. Accordingly, the possibility that two sub-groups of samples belong to the same population cannot be rejected.

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Behaviour of carboxylic acids on NH_4 -smectites: pollution prediction in waste landfill

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Waste storage induces environmental problems like soil and water pollutions by landfill leachates. Smectites are usually used as pollutant barriers at bottom of waste landfill. For this application, most interesting properties of smectites are their low permeability after compaction, expansion ability and high Cation Exchange Capacity (CEC). Waste decomposition leads to produce high amount of pollutants and it is necessary to predict the long-term behaviour of the clay barrier. Landfill leachates are first characterized by large amount of ammonium. Therefore a natural cation exchange can be predicted in clay barriers. Moreover, high amount of acetic acid are observed in landfill leachates. For these reasons we focused our study on acetic acid ($\text{pK}_a=4.74$) in interaction with ammonium montmorillonite, then extended to others carboxylic acids to better understand carboxylic acids and ammonium smectites interaction mechanisms. Experiments were performed with the reference SWy-2 montmorillonite totally exchanged with NH_4^+ cations and different carboxylic acids at several concentrations but higher than found in landfill.

NH_4 -smectite samples were stirred during 7 days in acetic acid solutions, then rinsed and dried at 40°C . The pH was controlled during experiments. Analyses performed by FTIR spectrometry indicate no adsorption of acetic acid onto montmorillonite. The main observed modification is a decrease of the H-N-H-bending intensity after acid treatment, which tends to decrease with the increase of acid concentration. Carbon, nitrogen and sulphur in the solid phase were quantified with a LECO CNS-2000 analyser. Nitrogen quantitative analyses indicate that ammonium cations are partially exchanged during the interaction with acetic acid. For example, 44% NH_4^+ cations were exchanged with 0.1 mol/L acetic acid ($\text{pH}=3.2$), although no carbon was fixed. Ammonium concentrations in solution after interaction were quantified with ionic chromatography, and confirm the partial cationic exchange of NH_4^+ by H^+ . Moreover, d_{001} reflection values have been measured by X-ray powder diffraction. In room relative humidity and temperature a shift from 1.19 nm for the sample before

treatment to 1.25 nm (cation exchange proportion=53%) was observed, corresponding to a NH_4^+ -to- H^+ exchange. These results are in accordance with the d_{001} reflection value of SWy-2 montmorillonite saturated by protons: 1.26 nm at 40% relative humidity (FERRAGE et al., 2005). Besides, the same general phenomenon was confirmed with the other montmorillonites of various CEC we studied.

Interactions between ammonium SWy-2 montmorillonite and other short-chain carboxylic acids (formic acid, $\text{pK}_a=3.75$; chloroacetic acid, $\text{pK}_a=2.86$; oxalic acid, $\text{pK}_a=1.25$) have also been investigated with the same protocol. At equal acid concentration, lower is the pK_a of acid, higher is the NH_4^+ -to- H^+ exchange rate. Furthermore, this study indicates that cation exchange is directly dependent on pH value for acid concentrations lower than 1 mol/l. Results showed that the behaviour of formic acid on ammonium smectite is very close to the one of acetic acid. The interaction is characterized by the absence of adsorption and only by the NH_4^+ -to- H^+ exchange. This exchange was also found when chloroacetic acid and oxalic acid were interacted with ammonium smectite. But in addition, we observed fixation on the clay with these two last acids, clearly characterized by an increase of the carbon concentration in the solid phase. These observations were confirmed by FTIR thanks to a stretching band in the C=O vibration range. Besides, XRD patterns showed a significant increase of d_{001} reflections from 0.5 to 2.5 nm which may be attributed to a fixation in interlayer space. Additionally, a decrease of the width at mid-height of the $00l$ reflections is observed for clay treated with oxalic acid, indicating a better stacking of the layers which can be attributed to a structural modification of the interlayer space.

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Barrier characteristics of clay and claystone: the BETTON database

Johannes GERARDI

The BETTON database (GERARDI, 2004) has been developed to provide data about the barrier characteristics of clay or claystones from Germany and other European countries to the members of the BGR clay research group. It can also be used as a tool for site characterisation, modelling, civil engineering and the clay working industry.

Geochemical, mineralogical, physical, mechanical and hydraulic properties determine the technical characteristics of clays and claystones. Corresponding data sets are stored in the database together with the lithological, stratigraphic and geographical descriptions, maps and significant illustrations. The database generally is to contain only data describing stratigraphic horizons. There are no spot samples, taken from any sequence or without reference to location and stratigraphy.

The geographical and stratigraphical position of the sampling site, the rock name and a layer description together with a site map and a photo of an outcrop are stored for each data set. The database contains sedimentological data, e.g. grain size, vitrinite reflexion data, lithological texture, REM images, and photographs of thin sections. The geochemical, mineralogical, and hydraulic data make up the main part of the database. Moreover, geomechanical, geophysical, and mineral properties, CEC, AEC, sorption and diffusion values, even having regard to anisotropic effects of the latter. Many values are presented as bandwidths and mean values. In these cases the respective raw data can be displayed in and exported into worksheet format (MS-Excel).

Data sources are numerous reports stored in the archives of the BGR and the state geological surveys of the Federal Republic of Germany. These reports deal with surveys and tests on disposal site selection projects or nuclear waste deposits, exploration of raw materials deposits, such as clay and hydrocarbons, as well as geological mapping

surveys. Other sources included in the database are open reports of scientific results provided by other scientific institutes, universities and from international joint ventures of the BGR in the field of the clay and claystone research. The sources of the data in the BETTON database are contained in a literature database. A glossary gives definitions of used terms.

The actual version of the BETTON database works as a client/server system. Using an MS-ACCESS 2002/2003 client on a Windows Server 2000 platform, the database is well embedded in the MS-Office environment. This enables the user to print or to export data, e.g. into MS-Excel or MS-Word and other data formats.

Data input by entitled users works with a special client. The integrity of the server hosted database is guaranteed by using different clients constructed as data input- and read-only clients. Plausibility checks are automatically conducted during the data input, particularly with regard to the correct order of magnitude of certain sensitive parameters.

BETTON provides user-friendly formats for the output of the results of a search for data. These formats can be used e.g. for data on a selected stratigraphic horizon at a selected site. Other formats are provided for the results of a search for the horizons in a given area with the properties of most interest with respect to barrier rock properties. Special formats are available for the output of a general overview on the data or in form of a strata log. As a future development of the BETTON database, the web presence is intended.

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1773: The year of the first manufacture of porcelain in Portugal

Celso de Sousa Figueiredo GOMES

The Portuguese were the first to introduce and commercialize in Europe the porcelain manufactured in China; however, within the European the Portuguese were the last to industrially produce porcelain, in 1835, in the Fábrica de Porcelana Vista Alegre. In Portugal, the first experiments of porcelain manufacture, at laboratory scale, were carried out in Lisbon by the engineer Bartholomeu da Costa, starting on 1773. We had the chance to analyse by XRD and SEM several of the manufactured porcelain pieces (medals and cameos) which are stored in the Museum of the Academia das Ciências de Lisboa. Mullite, cristobalite, cordierite, diopside and glass were identified as high temperature phases, the maximum firing temperature was estimated at 1300 °C, coal was used as fuel, and metallic en-

graved moulds were used in the conformation of porcelain pieces.

Figures 1a and b show the front and the back views of one of the studied porcelain pieces produced by Bartholomeu da Costa which is made of high quality porcelain, consisting mainly of mullite, glass being an accessory component. Kaolin of high purity was used as main raw-material.

Information relative to the composition of other porcelain pieces and to the raw-materials (kaolin, quartz sand, talc, calcite and dolomite) used in their manufacture will be disclosed.

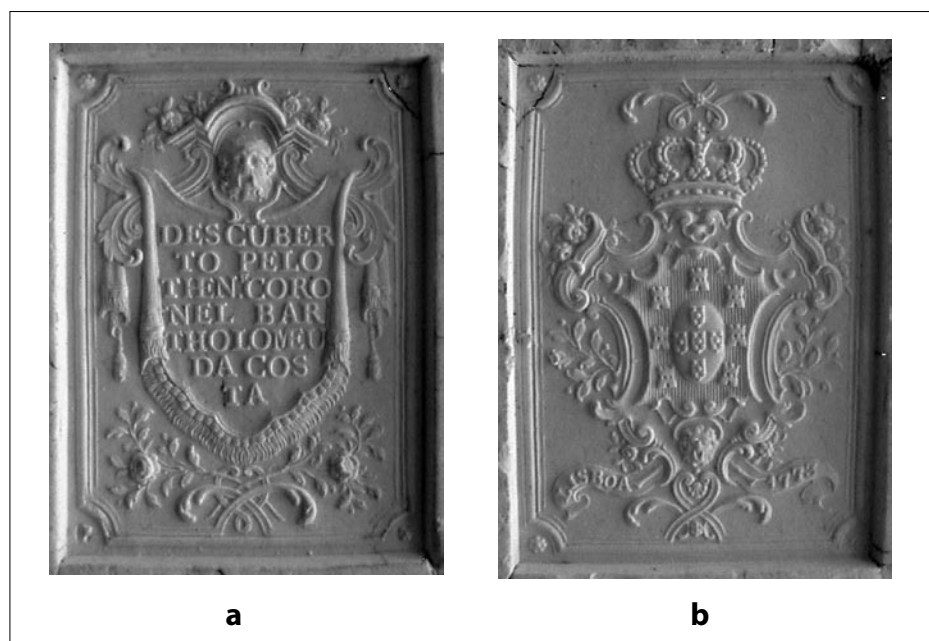


Fig. 1 Front (a) and back (b) views of the rectangular porcelain medal (5.5x4 cm) showing the Portuguese Royal Arms, the word Lisboa, and the date 1773.

Clay-based formulations to be used in topical applications

Celso de Sousa Figueiredo GOMES and Joao Baptista Perteira SILVA

Man and minerals are chemical systems having in common, in their composition, chemical elements which are essential both to life and to the formation of minerals. And, in the natural environment where man lives, both chemical elements and minerals are omnipresent. Therefore, interactions between man and chemical elements and minerals are expected to occur conditioning the living quality highly determined by the health state. These interactions can be classified as positive when they provide health benefits, or as negative when they are responsible for health risks, in both cases depending upon the dose/functional response. The intake of *minerals sensu latu (s.l.)*, concept that includes both *minerals sensu restrictu (s.r.)* meaning *natural inorganic solids*, and the *inorganic chemical elements*, can happen through ingestion, inhalation or absorption. The so-called *mineral salts* and *trace minerals* which are essential to life can be provided, either in diets, or in nutritional supplements. However, both *mineral salts* and *trace minerals* deficiency and excess can produce serious diseases of the muscular–skeletal, cardiovascular, gastro–intestinal, epidermal and endocrinal systems. On the other hand, certain *minerals sensu restrictu (s.r.)* can provide serious diseases too, for instance in the respiratory system, such as, silicosis and asbestosis. Clay, mud and other minerals have been used by man since the prehistory, in order to improve his health state, through internal (orally) and external (topically) applications. Clay and mud have spe-

cific natural properties, such as small particle size, platy or fibrous particle shape, varied chemistry and structure, high chemical inertia, hydrophilism, organophilism, high cation and anion exchange capacities, high adsorption and absorption capacities, high bio-adhesivity, high extensibility, high specific heat and low cooling rate, which make them interesting products for topical applications in balneotherapy, dermopharmacy and dermocosmetics. The natural properties referred to can be beneficiated and various application methodologies can be performed. Maturation is a current complex but essential process used to improve the properties of *peloids* for applications in *peloidtherapy* or *pelotherapy*. Recycling is another process of reusing the naturally scarce raw-materials used in *peloids* preparation, and of reformulating their composition.

This paper shows two examples of clay-based formulations which have been prepared for eventual use as complementary topical applications in the treatment of muscular–skeletal diseases. In such formulations besides specific clays and chemicals, other mineral resources (for instance, mineralo–medicinal water, biogenic carbonate sand and amorphous organic silica) participate in the formulations. These took into account the previously investigated specific properties of the minerals being involved which act as active principles, since they can liberate in a controlled manner some functional elements, such as, Ca, Mg, Sr, Si and S.

Physico–chemical and mineralogical characterization of the Hălmagiu clay (Arad county, Romania), a raw material for ceramic industry

Maria GOREA¹, Marcel BENEĂ¹ and Cristina MARIȘ²

Clays and kaolin represent the main raw materials for traditional ceramics, thus the identification of new resources is an important research direction in Romania, and in general. Among the new clay deposits of interest in this respect, we focused on the Pannonian clays from the Hălmagiu (Arad county) area.

The mineralogy and chemistry of the clays in the study area were investigated, followed by the technological characterization for establishing their best way of usage.

X-ray diffraction (on both unoriented and oriented samples), IR spectroscopy and thermal analysis were complementarily used in the view of establishing the mineral components, *i.e.*: kaolinite, montmorillonite-vermiculite, muscovite/illite, chlorites, carbonates (calcite), quartz, plagioclase feldspars, and Fe oxo-hydroxides.

The grain size distribution analysed by a laser granulometer has evidenced two fractions in the 0.5–10, and respectively 10–50 micrometers ranges, classifying the material as fine clay.

The physico–chemical transformations of the clay under thermal treatment, *i.e.* dehydroxilation of the clay minerals, carbonate decomposition, oxidation of Fe-rich minerals and formation of new phases etc., at temperatures of 700, 800, and 900°C have been evidenced by X-ray diffraction and IR spectroscopy.

For testing the technological characteristics (rheology of the slurry, water adsorption capacity, open porosity and apparent density), samples obtained by the wet method were thermally treated at temperatures of 900, 1100, and 1300°C. At 1300°C the melting process was complete, pointing out to optimal firing temperatures of 1100–1150°C. The colour of the fired product was brownish–red.

In conclusion, the Hălmagiu clay is recommended as main raw material for the construction materials industry (bricks), or, in smaller amounts, as additives for semi fine ceramics (wall and floor tiles).

The average chemical composition of the investigated clays is presented in the Table 1.

Oxides	LOI	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
wt %	15.73	46.90	0.58	16.29	6.08	11.72	1.30	0.30	1.40

Table 1 The average chemical composition of the investigated clays.

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The structure and diagenetic transformation of illite/smectite from marls of the Polish Flysch Carpathians

Katarzyna GÓRNIAK

Marls appear in western part of sedimentation basin of the Outer Carpathians among sediments indicating the beginning of flysch sedimentation on the turn of Tithonian and Berriasian (Silesian basin). In the eastern part (Skole basin) the initial stage of this sedimentation is marked by their appearance in Turonian. From this period till Eocene marly deposits occur both in the Skole and Sub-Silesian basins and from Eocene to Oligocene in the Magura, Dukla and Fore-Magura basins indicating the end of flysch sedimentation. Similar lithologic varieties of marls appear cyclically among sediments of different age.

These marls are strictly related to the palaeotectonic evolution of the Carpathians. Moreover, they are recording the evolution of sedimentation on the shelves of the Carpathian basins since these sediments are the effects of redeposition of shelf material to deeper parts of the Carpathian basins.

In the present study the following materials were investigated: Tithonian/Berriasian marls from the Silesian unit (Lower Cieszyn Beds), Upper Cretaceous marls from the Skole unit (Siliceous, Furoid and Węgiorka Marls) and Sub-Silesian one (Węglówka, Frydek, Jasienica and Żegocina Marls), Eocene marls from the Magura unit (Łącko, Budzów, Zembrzyce and Leluchów Marls) as well as Oligocene marls from the Dukla unit (Sub-Cergowa Marls) and from the Grybów one (Grybów Marls).

Natural samples and monoionic-saturated two separate carbonate-free fractions (<0.2 μm and 2–0.2 μm) were examined.

As follows from the obtained data, the Carpathian marls of different age from various tectonic units contain similar clay, dominated by smectitic mineral that displays a flaky form. Detailed studies of crystallochemical features of this mineral were carried out to reconstruct its origin and the course of diagenetic processes.

In these complex investigations the following methods were used: XRD (multispecimen technique), NMR, IR and Mössbauer spectroscopy, as well as chemical (FESEM/EDX, ICP) and thermal analysis (DTA-DTG-TG and EWA).

The obtained data indicate that smectitic mineral from the Carpathian marls is dioctahedral. It can be defined as high-smectitic, randomly interstratified mixed-layer illite/highly charged smectite. The ^{27}Al and ^{29}Si MAS NMR spec-

tra showing aluminium mainly in octahedral environment, as well as the results of Hofmann–Klemen's test indicating the localization of charge predominantly in octahedral sheet, allow to call the smectitic layers as montmorillonitic. This layer charge is due to the substitution of Mg^{2+} and Fe^{2+} for Al^{3+} . Moreover, the Mössbauer spectra indicate that a part of Al^{3+} is substituted by Fe^{3+} . Double dehydroxylation effect with the maxima below and above 600°C, observed in EWA curves, indicates the distribution of octahedral cations over *trans* and *cis* sites.

The analysis of the above presented data evidences that such features of octahedral sheet of the mineral studied as the presence of aluminium as the main cation, the occurrences of vacancies in *cis* positions, the substitution of magnesium and iron for aluminium causing the layer charge, indicate them to be primary properties of this mineral. They are characteristic for smectites formed by transformation of volcanic material (e.g. CHAMLEY, 1989; DRITS, 2003). Therefore, it is concluded that the precursor of smectite/illite occurring in Carpathian marls was volcanogenic smectite. The presence of non-swelling and of *trans-vacant* layers in its structure is the effect of diagenesis (DRITS, 2003). It is also postulated that the latter features is caused not only by illitization process but also the result of the change of geometry of octahedral sheets deformed by compaction and shear.

The observed coherence of the appearance of marls in the Flysch Carpathians with the stages of reconstruction of northern part of the Tethys Ocean and the results of crystallochemical examination of smectite minerals occurring in them strongly suggests the relation of tectonic activity with volcanic phenomena. Consequently, these geologically apparently mute marls can be considered as very useful tool for the reconstruction of palaeogeographic evolution of the Carpathians.

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Thermal properties of illitic material from Lower Carboniferous black shales (Western Pomerania, N Poland)

Katarzyna GÓRNIAK, Krzysztof BAHRANOWSKI, Adam GAWĘŁ,
Tadeusz RATAJCZAK and Tadeusz SZYDŁAK

Lower Carboniferous black shales of Western Pomerania are considered to be the source rocks of oil and gas deposits. The estimation of thermal maturity of these rocks is necessary to evaluate the possibility of generation of hydrocarbons within them. In this case the mixed-layer illite/smectite can be used as mineral geothermometer. Its proper use is conditioned by correct evaluation of origin of clay minerals contained in these rocks.

Dinantian black shales of Western Pomerania were formed in marginal part of extensional back-arc basin developed at the southern shelf of Fennoscandia. According to MERRIMAN (2005), volcanic material is a significant precursor of clay minerals in the basins of this type. In DRITS (2003) opinion, volcanogenic origin of smectitic precursor of mixed-layer illite/smectite formed during burial diagenesis is recorded in thermal properties of I/S, detected by evolve water analysis (EWA). This method was applied to confirm the primary presence of volcanogenic smectite as the precursor of illitic material occurring in the black shales studied. Volcanic origin of this precursor is suggested by common occurrence of volcanoclastic material in the whole cross-section of Dinantian deposits of Western Pomerania.

The black shales studied were sampled from two boreholes localized in tectonic blocks buried at various depth: Kurowo-1 in Drzewiany block and Żelazno-1 in Kołobrzeg one. Natural samples and Na⁺-saturated fractions (<2 μm and <0.2 μm) separated from them after removal of carbonates, were investigated using XRD, SEM/EDX, XRF, ICP methods, as well as thermal and evolved water (EWA) analyses.

Illitic material compose 49 to 71 wt.% of the black shales studied from both the mentioned boreholes. It displays a "cornflake" form. Some samples also contain chlorite (up

to 8 wt.%) and, locally kaolinite (up to 7 wt.%). The illitic material represents an ordered (Reichweite R=1–3), high-illitic mixed-layer illite/smectite, containing from 30% to less than 10% swelling layers. In some samples the presence of discrete illite as admixture cannot be excluded. Chemical analyses indicate some substitution of Al for Si in tetrahedral sheets of I/S and Mg and Fe for Al in octahedral ones. Apart from potassium, the main interlayer cation is calcium. Mixed-layer illite/smectite from black shales in Drzewiany block contains more swelling layers than that occurring in rocks of the Kołobrzeg block.

The examination of thermal properties (EWA) of illitic material of the black shales studied have evidenced two thermal effects at temperatures below and above 600°C, which can be assigned to dehydroxylation of *trans-vacant* (*tv*) and *cis-vacant* (*cv*) octahedral sheets respectively in illitic material. The presence of *cv* layers in diagenetic illite/smectite is considered to be the evidence of volcanic origin of its smectitic precursor. The formation of illite layers from smectite ones during illitization of the latter mineral leads to proportional increase of *tv* layers (DRITS, 2003). In the samples studied an interdependence between the content of swelling layers and the surface of the effects mentioned at the EWA patterns is observed. The surface of the peak at temperature above 600°C increases with growing content of swelling layers.

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Mineralogical and petrographical analysis of Kalenderberg household ceramic from Devín Castle (Slovakia)

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The Devín Castle is located in the southwestern Slovakia and represents a place of several remarkable archaeological findings. Among these, there are Early Iron Age ceramics artifacts assigned to the so-called Kalenderberg Culture (800–600 years B.C.) belonging to the northeastern Hallstattian cultural complex which overlapped partly the actual Austria, the most southern part of Moravia region in Czech Republic and the Sopron area in Hungary (STUDENÍKOVÁ, 1993). The Kalenderberg ceramics are typical for their shape as well as for the carved and painted decoration in geometrical patterns. The dominant vessel shapes are amphoras, situlas, conical bowls and bowls with shanks. They were all hand-made and they were used either as household ceramics or for burial ceremonies.

Twenty-four fragments of Kalenderberg-type household ceramic found at the Devín Castle were studied by mineralogical and petrographical analytical techniques that included plane-polarized light microscopy, X-Ray powder diffraction (XRPD) and scanning electron microscopy (SEM). Macroscopically, the ceramic shards can be classified into two categories: a) thin-walled, and b) thick-walled one. Shards colour is greyish or brownreddish. Sometimes transition of colours from brown–reddish to grey can be noticed. The XRPD patterns and the optical microscopy show that the ceramic shards are composed of clay minerals, quartz, plagioclase feldspars, K-feldspars, micas, carbonates and Fe-oxides. Based on the carbonate content – present either as limestone clasts or as fossils remnants, the ceramics samples were further classified into two groups. The firing temperatures were inferred from the mineralogical changes of the temper grains and from the matrix thermal alteration, i.e. vitrification–amorphization intensity, compared with references data, e.g. SHEPARD (1976).

Most likely the ceramics without carbonates content was fired in a range of 800–900°C ($\pm 50^\circ\text{C}$), while in the ceramic containing calcite, the firing temperature reached maximum 700°C.

The structure of the ceramic wall indicates modeling processes, as pressing several small clay lumps on a wooden form or by modeling from a single, almost spherical, clay lump opened with the fist or fingers (IONESCU & GHERGARI, 2002).

For the ceramics with carbonate content, the raw clays and temper originate most likely from loess sediments of the Devínska Kobyla Hill, located nearby the Devín Castle. On contrary, the raw materials used for the ceramics without carbonates content, might come from clayish sediments and alluvial sands of the Danube and/or Moravia river.

Acknowledgement: *In this way we would like to thank to the Geological Institute of Natural Science Faculty and the Central Laboratories for the Electric and Optic Methods from Comenius University of Bratislava for permission to use XRD and SEM facilities. Also we are very grateful to Dr. Corina Ionescu (Babeş-Bolyai University of Cluj-Napoca, Romania) for her help.*

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Experimental study of iron–bentonite and pyrite–claystone interaction at low temperature

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The principle of radioactive waste storage is based on a multi-barrier system consisting of two basic components – a geological and an engineered barrier. The metallic containers filled with vitrified nuclear waste are placed in an engineered barrier which is surrounded by a geological barrier. The reactive components of the engineered and geological barriers are clays (mainly smectites) while metallic containers could be made up of iron. To predict the long-term properties of these clay barriers, it is thus essential to study the interactions between clay minerals and iron.

Studies of the iron–clay interactions have shown the partial destabilization of the initial clay material and subsequent crystallization of reaction products (GUILLAUME et al., 2003; NEAMAN et al., 2003; WILSON et al., 2006). The nature of these reaction products depends on experimental conditions such as temperature, the nature of the initial clay material and others.

The present study deals with the interactions between bentonites, and more especially smectite, and iron (metallic Fe, steel plate) the last part of the study is focused on interactions between claystones, bentonites and pyrite.

The stability of bentonites in the presence of metallic Fe and steel plate was studied experimentally to simulate the mineralogical and chemical reactions of bentonites in contact with steel container in a nuclear waste repository. Bentonites from two Slovak deposits (Al–Mg montmorillonite and Fe–montmorillonite) were used as starting materials. Experiments were performed at 60 and 90°C for periods 5, 10, 15, 30 and 120 days, using bentonite, redistilled water, metallic Fe powder and steel plate. Both solid and liquid phases were analyzed. Solutions coexisting with the solid phases were analyzed by AAS, UV–VIS and pH measurements. Solid phases were characterized by XRD, SEM, FTIR and Mössbauer spectroscopy.

In the presence of metallic Fe powder, the experiments resulted in mineralogical changes in both starting bentonites. The XRD pattern of bentonites shows the origin of magnetite and significant decrease of smectite and feldspar reflections during experiments. After 30 and 120 days, a new reflection of metallic Fe is formed. During experiments with metallic Fe, the initial pH of the solution increases and redox potential (Eh) decreases considerably. The iron contents increase progressively in solution with the reaction time. Mössbauer spectroscopy demonstrates the consumption of metallic Fe powder in Fe–montmorillonite whereas in Al–Mg montmorillonite 41% of total Fe is present as metallic Fe after experiments.

In the presence of steel plate the steel surface oxidation was observed by SEM. In contact of the steel plate with Fe–montmorillonite the oxidation was more intensive than in Al–Mg montmorillonite.

Finally the stability of bentonites and claystones in the presence of pyrite was studied. Experiments were focused on the effect of pyrite on the claystone and bentonite stability. Experiments were performed at 80°C during different time periods.

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Vulcanized rubber filled with modified montmorillonite

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The development of polymer–clay nanocomposites has been creating a number of technologies and opportunities that can be applied to natural rubber (NR). NR nanocomposites have been prepared using procedures derived from those used for thermoplastics, based on mixing solid rubber with organoclays. The main aim for filler addition is to improve certain properties. The reinforcement of rubbers is expressed by enhancement of the mechanical properties (tensile strength and strain at break, modulus 100) of the vulcanizates; other properties, e.g. abrasion resistance are improving as well. The common natural clay, which is most often used as reinforcing agent, is montmorillonite, composed of silicate layers 1 nm thick and 200–300 nm in the lateral dimensions. In order to improve the clay dispersion in polymers, montmorillonite needs to be organically modified. This modification is achieved by substituting long-chain alkylammonium cations for the inorganic cations. The aim of the modification is to increase the inter-layer spacing and the hydrophobicity of the clay.

A commercial highly purified Na-montmorillonite (>98%) “Kunipia-F” (Kunimine Industries) of relatively high cation exchange capacity (119 meq/100 g) was used. The organic derivatives were prepared by ion exchange with octadecyltrimethylammonium (ODTMA), oleylammonium (OA) and octadecylammonium (ODA) cations. Polymer-layer silicate composites were prepared by direct

polymer melt intercalation; in some cases the mixtures of rubber and clay contained also silica as a conventional reinforcing filler. The effect of clay or organoclay loading from 1 up to 10 mass % on the tensile properties was measured. Stress at break, strain at break and modulus M100 were evaluated from the tensile tests. As expected, much higher values of mechanical properties are observed in the presence of silica. The stress at break of the materials systematically increases with increasing clay content. In the presence of silica, the organic cation in montmorillonite has negligible effect; but 15 mass % of SiO₂ increases substantially the stress at break values for all montmorillonite contents. The filler modification leads to higher values of strength and elongation compared to unmodified filler in the NR matrix. Modification of montmorillonite by different organic ammonium salts results in altered reinforcing and plasticizing effects of the filler in composites with rubber matrix. No difference between the materials with modified and unmodified filler is observed in the presence of silica. As with the stress at break results, similar trends for the strain at break data are obtained with 15 mass % SiO₂ in the polymer. Filler modification except for ODA leads to higher values of M100; negligible effect of the silica presence on M100 is observed for rubber/organoclay materials.

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Fast determination of CEC by Cu-trien method, its limitation and use

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Several methods have been suggested for estimation of cation exchange capacity of clays (CEC). All novel procedures to CEC estimation are focused on simplicity, low time demands, accuracy and repeatability. Cu-trien method was first proposed in 1999 (MEIER & KAHR, 1999). The method is based on interaction of highly charged small copper (II) cation with interlayer space of expanding clay minerals. During the exchange, the blue colour of Cu-trien complex is lightening. Exchange is reported to be fast and irreversible. Reaction time is short and consecutive treatment is not necessary. Measurable signal is developed within the exchange and easily measured – by UV-Vis spectrometry, or by AAS to avoid possible instability of the Cu-trien complex at varying pH (AMMANN et al., 2005) and possible problems with turbidity of the supernatant.

These advantages led to use of this method at our working place and test the influence of the type of cation in the interlayer space and stoichiometry and excess of the stock solution. Four homoionic (Ca, Mg, Na and Li) smectites with size under 2 μm from Rokle, Czech Republic, were prepared by step saturation by desired cation in 1 M solution, washed out by distilled water and finally followed by dialysis. Powder samples were well mixed and water content was determined by drying at 110°C for 24 hours. Three stock solutions were prepared with 0, 19 and 49% overload of trien over Cu(II). The loads of the stock solution were varied between 100 and 240% stoichiometry with respect to CEC of the samples. Reported UV-Vis detection was used and additionally AAS/AES spectrophotometry was applied to evaluate the cation balance in supernatant. Samples were prepared by dispersion of 0.11 g of clay in 10 ml of distilled water using ultrasonic bath. Consecutively the desired amount of stock solution was added and volume was fixed to 50 ml. After 15 min the suspensions were centrifuged or filtered and supernatant/filtrate was taken to analysis. The filtration was later excluded from the sample preparation procedure; not only to save time, but mainly because it caused Na^+ contamination and interaction of solution with paper itself is disputable. General trends observed are as follows:

Cationic balance in the supernatant is never reached which means that CEC determined by AAS/AES from cations sorbed and released is not identical. This fact can

be easily explained by heterogeneous occupation of the interlayer space although careful conversion to homoionic form was performed. Difference is larger with decreasing relative atomic mass of the interlayer cation. CEC determined from the balance of Cu^{2+} is recommended. Comparison of CEC determined by UV-Vis spectroscopy with CEC obtained by AAS of Cu^{2+} shows minor differences but attention should be paid at possible turbidity if UV-Vis is applied. The loads of stock solution influence the value of CEC estimated by Cu-trien. Oscillations increase with the use of stock solution of higher overload of trien and 1+ charged cations in interlayer space when both CEC AAS of Cu^{2+} and CEC UV-Vis have risen by 20 meq/100g.

Cu-trien method is a handy method for large series of samples (GRYGAR et al., 2005). It is recommendable to use exactly the same procedure of preparation of samples, ion exchange, and supernatant processing. For lower scattering of results stock solution with 1:1 ratio of Cu-trien should be prepared. UV-Vis spectroscopy is a quick way of determination of CEC, but possible turbidity can influence the results. AAS is powerful tool for determining CEC by determination of Cu^{2+} consumption. CEC determined from cations released is reliable only if all possible cations present in the original sample are determined and free calcite or salts soluble in neutral aqueous solutions are absent.

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Thermal alteration of mineral phases in Bronze Age ceramics from Transylvania (Romania)

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Potshards of Late Bronze Age (1400–1200 B.C.) hand-made pottery, exhumed in the archaeological site of Ilișua in North Transylvania (Romania) were studied by plane-polarized light optical microscopy (OM), X-Ray powder diffraction (XRD), thermal analyses (DTA), scanning electron microscopy (SEM), electron microprobe (EM) and electron paramagnetic resonance (EPR) in order to identify the phase components, their thermal alteration during the firing, and the raw materials. The ceramic fragments show in general a dark grey body colour, spotted by large white mineral clast and even pebbles as well as brick-red potshards. Across the wall thickness, the colour is rather homogeneous, only seldom a slight zoning with dark grey grading into reddish hues, can be noticed. The ceramic body is in general porous, due both to the elongated or irregular-shaped pores and to the microfissures.

The ceramics consists basically of a clayish matrix with combined, crystalline and amorphous fabric and exhibits different degrees of sintering and vitrification. In the matrix, variable amounts of magmatic, metamorphic and sedimentary lithoclasts, as well as various crystalloclasts, ceramoclasts and bioclasts are present. Granulometrically, based on the amount of Sm (small particles, between 0.02 and 0.5 mm), Md (medium size-particles, between 0.5 and 1 mm), Lg (large particles, over 1 mm), 55% of our samples classify as coarse ceramics while 45% can be assigned to the semifine one. The OM, SEM and EMP analyses reveal intimate thermal alteration processes, i.e. melting–diffusion–recrystallization, affecting mainly the matrix and its relationship with the clasts. The most important is the change of the clayish matrix, which forms a rigid body, where the particles are stucked together by sintering–melting processes. Fe migrated from the matrix into the softened rims of quartz grains. Parts of feldspar clasts became isotropic and the glassy, amorphous melt intruded into the cracks. New phases such as glass, gehlenite, wollastonite, hematite, anorthite, leucite, K-feldspar, and melilite formed as well. The burial alterations are marked by chalcedony deposition, analcime replacing the volcanic glass clasts and by P-enrichment.

Based on macroscopic and microscopic observations, as well as XRD, SEM, EPR and EMP data compared with reference data (MAGGETTI, 1982; DUMINUCO et al., 1998; RICCARDI et al., 1999; CULTRONE et al., 2001; BERTOLINO & FABRA, 2003, etc.) and with our previous experimental results, the firing conditions for the Late Bronze Age ceramics could be approximated in three large domains: 800–850, 850–950 and 950–1000°C. The mineralogical features of the matrix indicate that ceramics was obtained by mixing of kaolinitic–illitic and illitic–kaolinitic (\pm smectite) raw clays, with some iron-oxihydroxides content. The lack of calcite in the fired matrix as well as the scarcity of gehlenite and/or wollastonite indicates as well that they were non-calcareous clays or clays with only accidentally carbonate content. The clays came from at least two different sources, most likely located at hand. They were for example, the Badenian kaolinitic–illitic and illitic–kaolinitic clays occurring in the surroundings of Ilișua settlement. The high frequency of clay pellets reveal that some soil was added in the ceramic paste. The petrographic and mineralogical composition of the clasts points to the alluvial sandy sediments as tempering materials, derived from the Somes River flowing nearby the site.

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Cement suspensions for slurry cut-off walls with ultra fine ground Na-bentonite from Lieskovec and Jelšovský potok deposits

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Slurry cut-off walls are used as vertical barriers to control groundwater flow or to keep contaminants captured in waste containment systems. They consist typically of a mixture of selected bentonite, cement, additives and water. There is still a little information on long-term performance of cement–bentonite slurry cut-off walls. This paper is concerned with the research of rheological and utility properties of cement–bentonite suspensions and the examination of their durability potential. Laboratory immersion tests were performed to assess their chemical resistance.

The following materials were used for the tests: finely ground ($d < 45 \mu\text{m}$) Lieskovec and Jelšovský potok sodium bentonite and Portland cement of type CEM I 42.5 R. The suspensions were adjusted on the constant cement content per 1 m^3 and flow ability measured by the Marsh cone between 39 and 43 seconds. They were prepared by mixing water and bentonite until bentonite particles were fully hydrated. Cement was added afterwards and cement–bentonite suspension was constantly circulated until cement particles were fully dispersed. Bentonite portion differed between 16.5 and 13.2 mass % of the cement and showed varying percentage portions: the first comprises bentonite from Lieskovec (reference), while other mixtures consist of Jelšovský potok and Lieskovec blends in the ratios of 15 to 85, 22 to 78 and 30 to 70 mass %. Jelšovský potok has higher swelling ($W_L = 625\%$) than Lieskovec ($W_L = 300\%$) and served as upgrading agent. Water decantation was less than 1.5 vol. % per 24-hour sedimentation of the fresh sus-

pensions. Compressive strength varied between 0.72 and 0.88 MPa (cubes: $20 \times 20 \times 20 \text{ mm}$) after 28-day basic curing in water ($20 \pm 1^\circ\text{C}$).

Investigation of the effect of aggressive solution on hardened cement–bentonite suspension was performed using next principles: a) mixing the material with appropriate volumes of contaminants; b) evaluating utility properties (changes in weight, dynamic modulus of elasticity and strength); c) analysing reaction products (XRD, TG–DTA–DTG, SEM, chemical analysis) and d) immersing specimens in the solution of combined contaminants {0.05% MgCl_2 and 0.03% $(\text{NH}_4)_2\text{SO}_4$ solution containing following concentrations of aggressive ions: $\text{Mg}^{2+} - 127 \text{ mg.l}^{-1}$, $\text{Cl}^- - 372 \text{ mg.l}^{-1}$, $\text{NH}_4^+ - 82 \text{ mg.l}^{-1}$ and $\text{SO}_4^{2-} - 218 \text{ mg.l}^{-1}$ }. Compressive strength of the specimens ($20 \times 20 \times 20 \text{ mm}$) kept in reference water (W) and aggressive solution (AS) for one year is reported in Table 1.

The specimens showed negligible signs of attack – only some discolouration and fine softening of the surface on the edges of specimens (20 mm^3 and $20 \times 20 \times 120 \text{ mm}$) were observed after one-year exposure to aggressive solution; regularly restored. Valuable utility properties and high chemical resistance of suspensions to the combined contaminant were proved by the tests. The suspensions with ultra fine bentonite have been prepared for field applications.

Suspension No.	Curing	Compressive strength, MPa		
		28 days (basic)	180 days	365 days
1	W	0.88	0.91	1.02
	AS		0.81	1.20
2	W	0.72	0.98	0.97
	AS		0.88	1.00
3	W	0.78	1.03	1.01
	AS		0.78	0.99
4	W	0.75	1.01	0.94
	AS		0.94	0.99

Table 1 Compressive strength of cement–bentonite suspensions kept in water (W) and aggressive solution (AS). Specimens were kept for next 180 and 365 days in both liquids after basic curing.

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Correlation of organic and inorganic temperature indicators – a case study on low-temperature metamorphic rock series from Mt. Medvednica, Croatia

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In the last ca. 40 years numerous papers dealt with the physico-chemical controls of the organic maturation and the phyllosilicate reaction progresses acting during diagenesis and low-T metamorphism.

The aim of this work was to correlate inorganic and organic metamorphic grade indicators obtained on the Eoalpine (Paleozoic–Mesozoic) complex, the Jurassic ophiolitic mélange and Late Cretaceous–Paleocene sequence of Mt. Medvednica, Croatia (PAMIĆ & TOMLJENOVIĆ, 1998) providing additional data on the diagenetic–low-T metamorphic evolution of these rock series, the microstructural, mineral paragenetic and phyllosilicate “crystallinity” parameters of which were presented earlier by JUDIK et al. (2004).

For this purpose vitrinite reflectance, X-ray powder diffraction (XRPD)-based graphite “ordering” (LANDIS, 1971) and Raman spectroscopic parameters of the fine-dispersed carbonaceous material (CM) were used as thermal maturity indicators. Paleo-temperatures were calculated on random vitrinite reflectance (R_o) values using the equation of BARKER (1988) and on Raman spectral parameters based on the equations of BEYSSAC et al. (2002), RANTITSCH et al. (2004) and RAHL et al. (2005). Organic maturity data were correlated with the phyllosilicate “crystallinity” indices (illite Kübler and chlorite Árkai indices), apparent mean crystallite thickness and lattice strain values obtained by the Voigt method and results of the chlorite empirical Al(IV) thermometers and the geothermobarometer of VIDAL & PARRA (2000).

Fairly good correlation was proven between the temperatures calculated by empirical inorganic and organic “thermometers”. For anchi-epizonal metapelites from the Eoalpine (Paleozoic–Mesozoic) complex temperatures of ca. 300–420°C were estimated on the basis of mineralogical T indicators and R_o data. However, the Raman thermometers gave temperatures of ca. 390–460°C. In the Jurassic ophiolitic mélange R_o values suggested temperatures between 200–250°C. The Late Cretaceous–Paleocene sequence was characterized by peak temperatures of 100–230°C. T values increased systematically from youngest,

Paleocene towards the oldest, Cretaceous rocks. These data corresponded fairly well to the high temperature part of the diagenetic zone. The diagenetically altered rocks were characterized by superimposition of the Raman bands of the different CM generations. Therefore, the Raman thermometer can only be applied with caution in these rock series.

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The structure and chemistry of natural takovite and synthetic analogue of takovite

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The mineral takovite ($\text{Ni}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$) is an important nickel-containing phase in low-silica weathering deposits. Takovite and related minerals in the hydrotalcite group have structures in which brucite-like layers carry a net positive charge due to the substitution of trivalent for divalent cations (BISH, 1980).

The synthetic analogs of takovite, pyroaurite, and hydrotalcite are active heterogeneous catalysts of basic catalytic processes, such as oxialkylation, aldol condensations, etc. (KAPUSTIN, 1991). One can assume that natural minerals should have the similar properties. However, the distinction in the origin may have substantial influence on the ion-exchange and catalytic properties of natural and synthetic takovites.

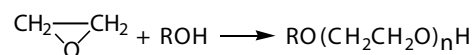
To compare the structure, physical-chemical properties, and catalytic activity of natural takovite and its synthetic analog, the latter was obtained by precipitation. This method involves the mixing of a concentrated, aqueous solution of Ni^{2+} and Al^{3+} with aqueous hydroxide-carbonate to yield an amorphous gel. At a final pH of 9–10, the carbonate concentration exceeded the stoichiometric requirements by a factor of approximately three. Following precipitation, the heavy gel was allowed to crystallize by heating for 24 h at 65°C. The aged gel was investigated by elemental analysis, thermal analysis and X-ray powder diffraction, and results were compared with those for the natural takovite. The presence of basic sites was examined on the surface of both natural and synthetic takovite by titration with benzoic acid in the presence of Hammett indicators. Because takovites have green color, the titration was carried out in the presence of white etalon for comparison. Bronsted basic sites of moderate strength were found on the surface of both synthetic and natural takovites, and the site distribution was dependent on the heat treatment.

The ion-exchange behavior was also studied for both natural and synthetic takovite. During the study of takovite we found that treatments with various dilute acid and salts solutions did not destroy the basic structure. The order of preference to inorganic ions was obtained from anion exchange experiments; synthetic and natural takovite both

showed pronounced preference for carbonate over other anions, which is also true for other minerals of pyroaurite and hydrotalcite groups. This makes the task of synthesizing non-carbonate samples difficult.

X-ray diffraction study reveals that ion-exchange of takovite with nitrate and chloride anions causes only minor changes in the structure, with minor increases in basal spacing. However, ion-exchange with sulfate anions leads to considerable change in basic structure and to formation of two different structures.

The catalytic activity of both natural and synthetic takovite was investigated in the reaction of alcohol oxialkylation. The reaction proceeds by a serial-to-parallel route resulting in the formation of a mixture of alkylene oxide addition products:



Our results show that in the kinetic region the reaction of takovite and alkylene oxide is first order. In the presence of both types of takovites the alkoxylation reaction proceeded similar to a basic-heterogeneously catalyzed reaction. In order to determine the influence of takovite's steric structure on its catalytic efficiency, the composition of reaction products was investigated. Both natural and synthetic takovite provided narrower product distribution in comparison with a homogeneously catalyzed reaction that is more typical of heterogeneous catalysis. These results can be considered in light of similarities and distinctions in structure and chemistry between takovite and its synthetic analogue.

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Detachment of colloids from bentonites in water

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Bentonites are currently investigated with respect to the applicability as geotechnical barrier for sealing radioactive waste e.g. in HLRW repositories (PUSCH, 1992). Their favourable properties are cation exchange capacity as well as swelling capacity in contact with aqueous solutions. The prerequisite for this application is the stability of bentonite under the expected conditions. Accordingly, several studies are available dealing with different scenarios of possible alteration processes (e.g. high pH, high salinity, extensive drying, etc.). In some concepts only a few possible candidate bentonites are investigated. However, it is well known that bentonite properties of different deposits or different parts of a deposit vary significantly. The dominating exchangeable cation (commonly either Na or Ca/Mg) is known to determine bentonite properties. In addition, the smectite content, layer charge density (distribution), chemical composition of smectites, morphology of (quasi)crystals and intergrowth between different components (amongst others) play a role.

This study was conducted in order to identify the differences of bentonite behaviour in contact with deionized water, representing the most simple aqueous solution.

As expected, Na dominated smectites readily disperse in water. Some of them liberate ultrafine colloids which

cannot be centrifuged even by using an ultracentrifuge with 20.000 U/min. Such colloids were particularly observed in case of 2 % w/w suspensions of Na dominated bentonites having pH values >9. After centrifugation the supernatant containing the colloids was separated. The colloids were enriched by evaporation and analyzed by ESEM, XRD, and IR. All three methods prove that the colloids are mainly smectites, although minor amounts of X-ray amorphous phases might be present.

We propose that bentonites which react alkaline in contact with water tend to liberate colloids due to weakening of chemical bonds caused by the high pH value (according to solubility of silicates depending on pH) and by the higher reactive surface area of Na smectites in suspension.

We conclude that such bentonites are less suitable for the application as geotechnical barrier in HLRW repositories since they tend to liberate colloids which: (a) are able to transport radionuclides as colloidal complexes and (b) reduces the mass of the geotechnical barrier itself.

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Geochemical studies on pore water from two different clay types in the frame of radioactive waste disposal researches

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Argillaceous formations ranging from plastic clays (Boom Clay, Belgium) to highly consolidated claystones (Boda Claystone Formation, Hungary) are considered as promising host-rocks for the geological disposal of high-level radioactive waste.

In the last decades important research efforts and analyses were made both in Belgium and Hungary in the field of radioactive waste disposal. To assess the safety of the clays as a geological barrier, a good understanding of the mineralogical and geochemical composition of the clays, as well as the mechanisms controlling the geochemistry of their pore waters are essential as it reveals the geochemical stability of the host rock and influences the migration/retention of radionuclides.

Geochemical studies conducted in the last years on the Boom Clay at the SCK-CEN (Mol, Belgium) used different pore water extraction techniques: *in situ* sampling using piezometers in the HADES Underground Research Facility (Mol, Belgium), and laboratory extraction techniques such as squeezing and leaching (DE CRAEN et al., 2004). Beside the determination of the chemical composition, Eh, pH and pCO₂ of Boom Clay pore water, studies started on the composition and stable isotope composition of the dissolved gasses in the Boom Clay pore water (KELE et al., 2006). Using the PEGASUS experimental set-up (MOORS et al., 2005) it was possible to take samples and measure

the above mentioned parameters under undisturbed *in situ* Boom Clay conditions.

In the case of the Boda Claystone, piezometer-derived pore water is not available. Furthermore, the squeezing technique could not be used because of the low pore water content in this claystone (1 wt %). Therefore, the leaching technique is used to study the pore water composition of the Boda Claystone. This study started recently and only preliminary results are available yet.

The aim of this work is to present and compare the experiences of sampling techniques and geochemical analyses of pore water from two different clay-rock types to provide information for the radioactive waste disposal researches.

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The synthesis of iron-containing pillared clays from natural clays of Transbaikalia and research of their catalytic properties in wet oxidation of phenol by hydrogen peroxide

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Fe/Al-modified clays prepared by pillaring voluminous metallic complexes between structural layers of swelling clays, such as montmorillonites, were used as heterogeneous catalysts for oxidation of toxic organic compounds (GUELOU et al, 2003; CARRIAZO et al, 2003).

The Fe/Al-modified clays catalysts were synthesized from naturally occurring montmorillonites, located in Taryat, Zagustai and Mukhortala (Transbaikalia, Russia) and were called Fe/Al-T, Fe/Al-Z and Fe/Al-M, accordingly. The modification of clay was carried out by exchanging interlayer ions with polyoxocations containing iron and aluminum $[\text{FeAl}_{12}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ with like Keggin structure. The pillaring solutions of Fe/Al were prepared by mixing appropriate volumes of aqueous 0.1M Fe and Al chlorides with 0.1M NaOH to obtain a final solution of molar ratio Fe/Al = 1/10. The molar ratio OH/metal was 2. Solution, containing Fe/Al polyoxocations, was added to the dispersion of the clay (1%) at 80°C, the mixture was stored overnight at room temperature. The clay was previously treated by ultrasound during 3 min at 22 kHz. The pillared clay was washed with water, filtered by suction, dried in air and calcined at 500°C. The iron content of these catalysts was to average: Fe/Al-T – 1.9%, Fe/Al-Z – 3.6% and Fe/Al-M – 1.6%.

The obtained catalysts were studied in the wet reaction of phenol oxidation by hydrogen peroxide. The conversion of phenol on all catalysts achieved 100% and rate of phenol oxidation decreased in a following order: Fe/Al-M > Fe/Al-Z > Fe/Al-T. Whereas leaching iron ions on Fe/Al-Z (13.3%) was more than on Fe/Al-T (2.0%) and Fe/Al-M (1.5%) those according to content iron in catalysts. Thus, Fe/Al-M possesses the best technological adjectives: the high rate phenol oxidation and the low leaching iron ions.

The main textural characteristics of Fe/Al-M were measured by nitrogen adsorption at 77 K: BET surface area

– 219 m²/g, pore volume – 0.270 cm³/g, pore diameter – 37 Å. The d_{001} -spacing, determined by XRD analysis, showed that interlayer was 18 Å.

The kinetics behaviour of phenol oxidation was studied on catalyst Fe/Al-M by varying the reaction temperature from 40–60°C, pH 2–6, hydrogen peroxide concentration 0.25–25.0 mmol/l, phenol concentration 0.25–4.0 mmol/l and catalyst 0.5–5.0 g/l. The intermediate products detected by HPLC were hydroquinone, catechol and carboxylic acids. The carbon dioxide and water were determined as the final products. It was shown that the reaction temperature, concentration of hydrogen peroxide, phenol, catalyst and pH influenced the phenol oxidation. It was established that the initial rate of the reaction, as well as the leaching of iron ions in the solution, increased with the increasing concentration of reagents. The maximum oxidation rate of phenol was achieved at pH = 3.7–3.9. The optimal conditions of reaction of phenol oxidation were established: $t=50^\circ\text{C}$, $\text{pH}=3.7-3.9$, $[\text{PhOH}]:[\text{H}_2\text{O}_2]=1:14$ mol/mol and the catalyst content 1 g/l.

The high catalytic activity and high stability of Fe/Al-M in the reaction conditions allows us to consider it as a perspective catalyst for sewage treatment from phenols.

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Structural heterogeneity of alkylammonium-exchanged synthetic swelling fluoromicas

Zenon KŁAPYTA

Swelling fluoromicas can be synthesized from the mixture of suitable oxides and fluorides melted at 1300–1500°C or from talc using an intercalation procedure. These silicates are produced on the industrial scale and, in comparison to natural clays, show a greater degree of crystallinity. Their chemical composition and physico-chemical properties can be controlled in a wide range.

Alkylammonium derivatives of clay minerals have been extensively studied. In contrast, surprisingly few investigations have been reported on the adsorption of organic ammonium ions on synthetic layered silicates. In this work, two synthetic swelling micas: Na-fluorotetrasilicic mica (TSM) and Li-fluorotaeniolite (TN) were used as starting materials. Their cation exchange capacities (CECs), determined by adsorption of alkylammonium ions are 92 and 124 meq/100 g.

Organo-micas were prepared by ion exchange with dodecyl-, tetradecyl-, hexadecyl- and octadecyltrimethylammonium (C12, C14, C16 and C18) bromides. Concentration of the ammonium salt varied from 0.25 to 4.0 CEC of the mica. The products were characterized using ^{23}Na MAS NMR spectroscopy, X-ray diffraction (XRD) and C and N determinations.

As shown by ^{23}Na MAS NMR, up to 25% of the total amount of Na^+ ions in the TSM were non-exchangeable, even if a large excess of the organic salt was used. The maximum amount of the alkylammonium ions adsorbed on the mica was 92 meq/100 g. However, at high concentrations of the C16 and C18 surfactants, it was found that, except for organic ions, the salt molecules were additionally adsorbed on the silicate, resisting washing with water but being removable with ethanol.

The XRD patterns of the samples obtained show that the alkylammonium ions are distributed inhomogeneously

within the mica interlayers. As a consequence, the organo-TSMs contain several phases consisting of randomly and regularly interstratified layers differing in terms of the amount of the alkylammonium ions adsorbed. The largest basal spacings (40.8–50.4 Å) indicate the presence of a superstructure, composed of two different layers. However, these layers swell in ethylene glycol in the same manner and form new interlayers with identical spacings. From the XRD patterns it is clear that the organo-TSMs do not contain the Na-TSM phase and the interlayers are presumably filled with both organic and Na^+ ions in various ratios.

The maximum amount of the alkylammonium ions adsorbed on the TN was 124 meq/100 g. By reacting the mica with an excess of the C16 and C18 salts, the surfactants were adsorbed in both cationic and molecular forms as it was found for TSM. Thus, the interlayer Li^+ ions were also only partially replaced by the alkylammonium ions.

The XRD patterns of the organo-TNs show a series of reflections suggesting that the samples obtained are polyphasic. The strong peaks in the range 23.3–28.7 Å may be ascribed to the random interstratifications of the TN layers with diversified amount of adsorbed alkylammonium ions. The peaks with very low intensity corresponding to the basal spacings of 42.3–51.2 Å indicate that small amounts of regularly interstratified layers are present.

This study also shows that adsorption of ethylene glycol, well known and widely used in clay mineralogy, may be successfully applied to XRD characterization of alkylammonium-exchanged silicates, especially those with mixed-layer structure.

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Intercalated montmorillonites by different aggregates of methylene blue

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Using Vis-absorption spectra of methylene blue (MB) in aqueous solutions the equilibrium aggregation constants β_q of the q -th dye aggregates were evaluated. From these data the distributions of dye monomer, dimer, trimer and tetramer were calculated for aqueous solutions with different MB analytical concentration. The montmorillonite samples (Na-SWy and Ca-Cheto) were fully intercalated with MB aqueous solutions of various ratio monomer/dimer/trimer/tetramer. The adsorbed amount of MB in fully intercalated montmorillonite samples (MB-SWy and MB-Cheto) was calculated from total analyses of these samples. The molar ratio MB/montmorillonite increases from 0.536 to 0.685 mol/mol for MB-SWy and from 0.896 to 1.124 mol/mol for MB-Cheto with increasing concentration of dye in aqueous solutions. These data are in good agreement with CEC that is much higher for Ca-Cheto (1.50 meq.g⁻¹) in comparison with Na-SWy (0.88 meq.g⁻¹).

Moreover there is a very good positive correlation between molar ratio MB/montmorillonite and basal spacing d_{001} of fully intercalated montmorillonite samples (MB-SWy and MB-Cheto).

Structure analysis using combination of diffraction data with molecular modelling revealed the differences in the interlayer arrangement of MB⁹⁺ guests in SWy and Cheto montmorillonites. Fluorescence measurements showed the strong effect of the silicate layer charge on the spectroscopic behavior of MB⁹⁺ guests intercalated in montmorillonite. Methylene blue exhibits the strong luminescence in MB-SWy and almost no luminescence in MB-Cheto samples.

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Table 1 Characteristics of intercalated montmorillonite samples with methylene blue. Notes: c – analytical concentration of MB in aqueous solution; \bar{q} – mean q -th MB⁹⁺ aggregate in aqueous solution; d_{001} – basal spacing of fully intercalated montmorillonite sample; MB/MMT – calculated molar ratio between MB and SWy or MB and Cheto; q_{MB} – intercalated amount of MB (meq MB/g Na-SWy or meq MB/g Ca-Cheto); q_{sum} – sum of Na, K and Ca (meq Alk/g Na-SWy or meq Alk/g Ca-Cheto); $q_{sum} = q_{Alk} + q_{Alk^*}$

Sample	c (mol/l)	\bar{q}	d_{001} (nm)	MB/MMT (mol/mol)	q_{MB} (meq/g)	q_{Alk} (meq/g)	q_{sum} (meq/g)
MB-SWy(II)	5.00.10-5	1.10	1.51	0.536	0.71	0.34	1.05
MB-SWy(III)	2.00.10-4	1.34	1.53	0.528	0.70	0.22	0.99
MB-SWy(IV)	5.00.10-4	1.59	1.54	0.581	0.77	0.13	0.90
MB-SWy(V)	2.00.10-3	2.05	1.55	0.585	0.78	0.19	0.97
MB-SWy(VI)	5.00.10-3	2.39	1.58	0.685	0.91	0.18	0.99
MB-Cheto(II)	5.00.10-5	1.10	1.71	0.896	1.21	0.32	1.53
MB-Cheto(VI)	5.00.10-3	2.39	1.86	1.124	1.52	0.22	1.74

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Sorption of arsenic on clay minerals – a theoretical approach

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The mobility of arsenic species in the environment is largely controlled by solid phase sorption reactions (LANGMUIR, 1997; WILKIE et al. 1998). Quantitative evaluations of the solid phase/water partitioning of many toxic metals, including arsenic, are best accomplished by a surface complexation approach (CHERRY et al., 1986; SADIQ, 1997). Equilibrium-based thermodynamic modelling is currently one of the most appropriate methods to evaluate the competitive geochemical processes that affect the transport and toxicity of arsenic, including predictions regarding arsenic persistence and mobility in the environment.

The numerical computer code PHREEQC was used to simulate arsenic surface complexation from a small watershed with naturally high levels of arsenic on clay mineral components (kaolinite and montmorillonite) of a stream sediment. Surface complexation mass-action coefficients were obtained from the literature in the generalized two-layer model form, or from linear free energy relationships. A reasonable simulation of expected arsenic concentrations is obtained using competitive complexation, literature-derived sorption constants and the PHREEQC model.

The USGS computer code PHREEQC version 1.6 was used for all simulations. The WATEQ4F thermodynamic database formed the core to which surface complexation parameters were added. The code was used for the calculation of saturation indices, sensitivity analysis of parameters such as Eh, pH and temperature, modelling the mixing of stream water of different compositions. The surface complexation routine was used in the generalized two-layer

model and competition between arsenic and other ions for sorbing phases for a finite number of sites was allowed. Both mineral assemblages were allowed to come to equilibrium by simulating the flushing of many pore volumes through the sediment–mineral surface assemblage. The model output was evaluated using the ratio “R” of modelled vs. expected arsenic concentrations.

Small differences in the conceptual model and data acquisition techniques can have a large effect on the simulation error. The error of neglecting competition by common compounds such as bicarbonate or silicic acid can equal or exceed the bias resulting from inappropriate choice of mineral phases. The continued development of field and analytical protocols to support surface complexation modelling is clearly needed.

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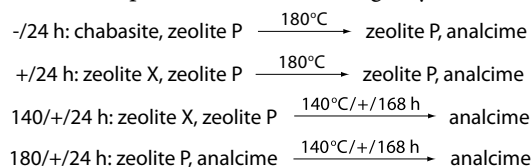
Hydrothermal stability of geopolymers

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Geopolymers represent network structures of alkali-activated metakaoline relicts produced in the presence of water-glass. According to Davidovits, the author of the original patents, geopolymers can be considered not only as a full-value substitution of cement bonding agents, but according to his hypothesis, even old Egyptians used these materials in building pyramids based on simple reactions of raw materials available at that time (DAVIDOVITS & DAVIDOVITS, 1999).

Blocks with dimensions 2x2x2 cm were prepared from mixtures of metakaolin, water-glass and alkali in systems $(1.1-1.2)\text{Na}_2\text{O}-(3.6-4.4)\text{SiO}_2-\text{Al}_2\text{O}_3$ and $1.2\text{K}_2\text{O}-4.4\text{SiO}_2-\text{Al}_2\text{O}_3$. The composite materials were subjected not only to normal ageing, but also to hydrothermal exposition in an autoclave at 100, 140 and 180°C with/without aqueous medium for 24 hours, or in aqueous environment for 168 hours. The original compressive strengths were about 14 MPa and 26 MPa in the Na_2O and K_2O environments, respectively. After the hydrothermal exposition, the compressive strength of the Na composites gradually decreased to 4 MPa in the longest experiments, but already after one day at 100°C it decreased to half of the original value. The compressive strength of geopolymer can be correlated with formation of zeolite phases, however, their relation is ambiguous. Although the sample strength decreases more in the aqueous environment than in the system without added water a higher enrichment in the zeolite phases has been found. In the experiments at 100°C, zeolite mineralization has not been observed. In the higher temperature systems, kinetically stable zeolite forms have been formed, e.g. zeolite P and analcime in addition to the metastable zeolites X

(faujasite) and chabasite. The result of hydrothermal syntheses can be expressed in the following way:



No zeolite mineralization has been found in the products of K-geopolymers, and this has probably been the reason for their higher compressive strength after the hydrothermal exposition.

The Na-geopolymers were further subjected to a nearly half year autoclave exposition at 60°C in the aqueous environment. The original compressive strength decreased from 28 MPa to 14 MPa. The presence of the zeolite bound water has been confirmed by DTA curves. In the ²⁹Si MAS NMR spectra, the intensity of the Q4 (3Al) signal characteristic for geopolymers (as well as their compressive strength) decreased while the intensities of the P-zeolite signals associated with higher Si/Al ratios increased.

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Iron phases occurring in Fe-rich bentonite from Lieskovec, Slovakia

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Fe-montmorillonite of relatively low charge is the dominant mineral in Lieskovec bentonite (Central Slovakia) developed from andesitic pyroclastics. Admixtures of kaolinite, quartz, cristobalite and plagioclase are present in all samples, while muscovite/illite and orthoclase occur in most samples. The Lieskovec bentonite deposit is relatively homogeneous as demonstrated by quantitative analysis using Rietveld refinement, though some differences in the samples obtained from different parts occur. Size fractionation failed to separate pure smectite. The <2 μm fractions contain smectite, kaolinite and traces of crystalline non-clay minerals. Total contents of SiO_2 , Al_2O_3 and Fe_2O_3 in the raw bentonite samples are 53–65, 16–22 and 5–9 %, respectively. The Fe_2O_3 content in Lieskovec bentonite is higher than in most other Slovak bentonites. Preliminary data obtained from Mössbauer spectra taken at room and liquid nitrogen temperatures show that Fe(II) content is low and Fe(III) occurs dominantly in smectite. Goethite and/or hematite, containing up to 26 % of total Fe, are present in some samples (ANDREJKOVIČOVÁ et al., 2006).

Results of most recent variable temperature Mössbauer spectroscopic assay of Lieskovec bentonite and its <2 μm fraction will be discussed.

The hyperfine parameters of the Mössbauer spectra for raw bentonite L3 (Fig. 1) are consistent with structural Fe(III) in an aluminosilicate phase mixed with an Al-substituted hematite. The hematite did not undergo the Morin transition, as evidenced by the negative values for the quadrupole splitting of -0.264 mm/s at 30 K and -0.158 at 6 K. The intensity of the sextet relative to the doublet increased from about 10% to about 15% between temperatures of 30 and 6 K. The magnetic hyperfine field of >52 T at both temperatures is consistent with an Al-substituted hematite but it is too high for ferrihydrite, goethite, or maghemite (MURAD, 1988, 1989).

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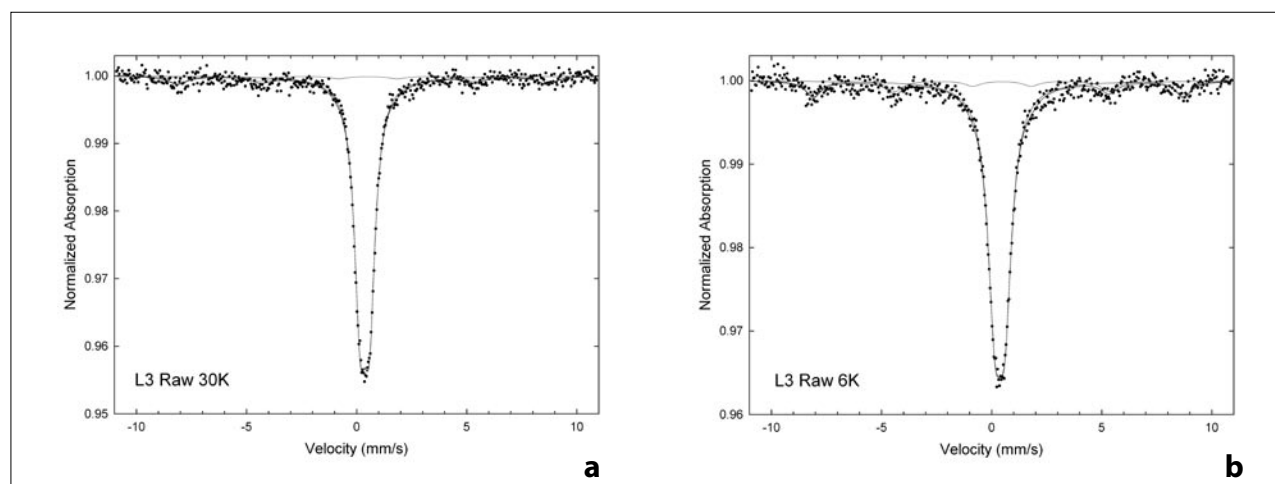


Fig. 1 Mössbauer spectra of Lieskovec bentonite sample L3 at 30 K (a) and 6 K (b).

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Chemical compatibility of GCL mineral component to site-specific liquid

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Geosynthetic materials such as geomembranes and geosynthetic clay liners (GCLs) are frequently used in composite clay liners for landfills. In line with ASTM recommendation the clay portion of a GCL should be tested for chemical compatibility to liquids. A series of mineral composition, swell index, fluid loss and water absorption capacity tests of bentonite were conducted. The site-specific liquid i.e. real leachate was collected from the leachate retention basin of a municipal solid waste disposal site Jakuševac near Zagreb.

Besides the baseline testing performed on “as-received” samples (series I), three other series of tests were also made. GCLs mineral component (bentonite) was immersed into the leachate during different periods of time for two series (II and III), after what index tests were performed using demineralized water as a test fluid. The last series of experiments (series IV) was conducted using the site specific liquid as a test fluid.

Water absorption test results are shown in Fig. 1. The results indicate the decrease of absorption capacity with the increase of sample immersion time into the leachate: the longer immersion period, the smaller absorption capacity.

Test results for fluid loss yield no significant difference in values obtained with “as-received” samples in comparison with samples immersed into the site specific liquid.

Free swell test results are shown in Table 1. The results for samples immersed into the site specific liquid (series II and III) show the increase of swell index with the duration of immersion comparing to baseline testing (series I). On a contrary, the tests performed with site specific liquid as test fluid (series IV) show much lower swell index.

Mineral composition has been determined by X-ray powder diffraction (XRD). XRD analyses indicate that the sample contains about 75% of clay minerals with majority of the minerals being smectite. The change of basal spacing is noticed for samples immersed into the leachate. It is also interesting to note that these changes occurred immediately after immersion because the results of series II (7 days) and series III (60 days) do not show almost any difference.

XRD analysis and index tests conducted on specimens immersed into the site specific leachate during different periods of time showed some influence of leachate to the bentonite behaviour. However, swell index tests conducted using the site specific leachate as a test fluid showed significant influence of leachate to the bentonite.

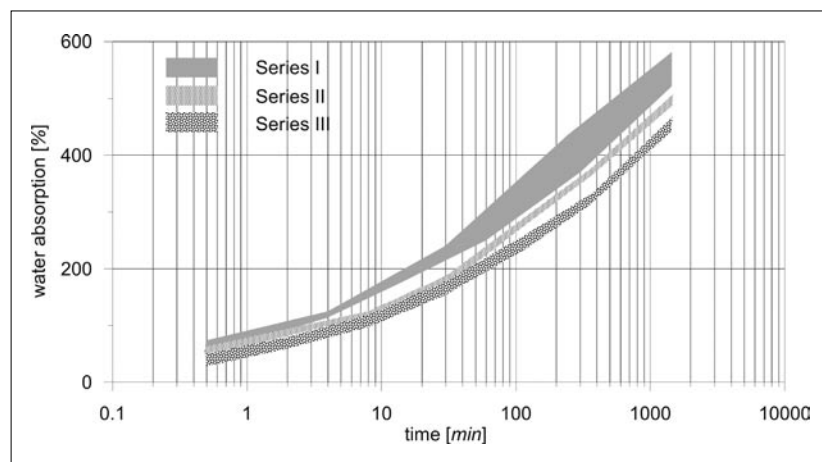


Fig. 1 Water absorption capacity.

Table 1 Swell index [ml/2g]. Legend: series I (“as-received”); series II (immersion time – 7 days); series III (immersion time – 60 days); series IV (leachate as test fluid).

Sample no.	Series I	Series II	Series III	Series IV
1	34	35	44	16
2	33	34	43	16.5
3	34	34	43	16

Geochemistry and weathering of the Late Cenozoic red clays in the Pannonian Basin

János KOVÁCS

During the past decade little attention has been paid to the red clays in the Pannonian Basin. Important key formations in the Late Cenozoic stratigraphy are the red (silty) clays. Litho-, bio-, chemo- and magnetostratigraphic data show that they formed in different periods (SCHWEITZER & SZŐÖR, 1997; VICZIÁN, 2002; KOVÁCS, 2003). The youngest red paleosol (reddish clay) is of Early Pleistocene age. The older one (red clay) was formed in the Early and Middle Pliocene (PÉCSI, 1985; KRETZOI, 1987; SCHWEITZER & SZŐÖR, 1997; KOVÁCS, 2003).

Geochemical study was carried out on 50 samples from 14 red clay sequences. The red clays are primarily composed of silt and clay (KOVÁCS, 2003, 2006). Degrees of chemical weathering during the Pliocene were estimated by using geochemical proxies including CaCO_3 contents, chemical index of alteration ($\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$) diagrams (NESBITT & YOUNG, 1982) and mineralogical index of alteration (MIA) (VOICU et al., 1997). The degree of silicate weathering can be estimated by the chemical index of alteration (CIA). These values are 60 to 90, which show a strong weathering process. The mineralogical index of alteration evaluates the degree of mineralogical weathering, i.e. the transformation ratio of a primary mineral into its equivalent alteration mineral. It has the advantage of indicating the degree of weathering for each analyzed sample, independently of the depth of sampling. The MIA values of our samples (60–100%) indicate intense to extreme weathering. The value of 100% means complete transformation of a primary mineral into its equivalent weathered product and, by extrapolation, complete weathering of the parent rock.

The degree of chemical weathering can be estimated by geochemical proxy indicators. Elemental concentrations such as K, Na, Ca, Sr, Ba and CaCO_3 as well as element ratios of K/Na, Al/Na, Rb/Sr, and Sr/Ba have been widely used to study the degree of chemical weathering based on the fact that these elements commonly display remarkably different mobility and are fractionated to different degrees through chemical weathering (DING et al., 2001; YANG et al., 2006). Our data show high ratios of K/Na, Rb/Sr, and

Al/Na and low Sr/Ba ratio, which indicate strong chemical weathering because Na and Sr are more mobile than Al, K, Rb, and Ba and consequently easily removed from parent rocks during chemical weathering.

The results show that chemical weathering was intense in the Pannonian Basin in the Late Neogene.

The CIA and MIA values suggest that warm and humid climate was predominant and responsible for the intense chemical weathering. The weathering values suggesting that the Neogene palaeoclimate in the Pannonian Basin was more humid and hotter (thus favoring intense chemical weathering) compared to the present climate regime.

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Thermal behaviour of synthetic takovite-like anionic clays studied by high-temperature X-ray diffraction and Raman spectroscopy

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Anionic clays (layered double hydroxides, LDHs) with hydroxalite-type structure are often used as precursors to obtain mixed oxides applicable in heterogeneous catalysis. Three takovite-like anionic clays with chemical composition of $\text{Ni}_{1-x}\text{Al}_x(\text{OH})_2(\text{CO}_3)_{x/2} \cdot y\text{H}_2\text{O}$ and Ni/Al molar ratio of 2, 3, and 4 were prepared by coprecipitation of nitrate solutions. A part of prepared samples was hydrothermally treated for 20 h at 180°C. Thermal decomposition of prepared products and phase transformation of formed Ni–Al mixed oxides were studied using thermal analysis (TG/DTA/EGA), high-temperature X-ray diffraction (HT XRD) and Raman spectroscopy.

A hydroxalite-like phase of relatively low crystallinity was present in the coprecipitated products. After hydrothermal treatment, an increase of integral intensity and significant decrease of FWHM values of hydroxalite diffraction lines were observed, which indicate an improved crystallinity of LDH phase. No other crystalline phases were found in coprecipitated or hydrothermally treated samples. For the sample with Ni/Al molar ratio of 4, the effect of hydrothermal treatment was not significant.

Two major endothermic effects characteristic for hydroxalite-like compounds were observed in DTA curves. The first endothermic effect accompanied by H_2O evolution was found at 200–250°C and it was ascribed to the release of interlayer water. The dehydrated samples retained the layered hydroxalite structure with slightly decreased basal spacing. A formation of such low-temperature metaphases after heating of LDHs was reported formerly by STANIMIROVA et al. (1999). The corresponding shift of (003) diffraction line in HT XRD measurements was found at temperatures of about 50°C lower in comparison with results of thermal analysis. The second endothermic effect was observed at 320–380°C and it was accompanied by a simultaneous evolution of H_2O and CO_2 . The HT XRD measurements showed a destruction of LDH structure at these temperatures and a gradual formation of NiO-like phase above 350°C. The hydrothermally treated samples exhibited both dehydration and decomposition temperatures of about 30°C higher in comparison with coprecipi-

tated samples without hydrothermal treatment. Thermal stability of prepared LDHs decreased with increasing Ni/Al molar ratio.

The NiO-like phase was formed after thermal decomposition of takovite-like LDHs. The lattice parameter of NiO-like phase was slightly lower in comparison with reference NiO, which can be explained by presence of Al ions in the NiO lattice. The NiAl_2O_4 spinel was detected together with NiO in powder XRD patterns of samples calcined at high temperatures above 900°C. On the other hand, the full-profile fitting of XRD patterns indicated a trace amount of spinel-like phase in the samples obtained even at relatively low temperature of 400°C. The Raman spectra of samples calcined at 400°C were nearly coincident with spectrum of reference nickel oxide. The major band at about 550 cm^{-1} is related to Ni in octahedral coordination. The corresponding bands were found also in Raman spectra of takovite-like LDHs. The complex band with maximum at 550 cm^{-1} characteristic for NiO can be fitted using three separate bands. The Raman spectra of calcined takovite-like LDHs were also fitted using these three bands and their gradual sharpening with increasing calcination temperature was observed. In the Raman spectra of samples calcined at 800°C and higher temperatures, the new band at ca. 600 cm^{-1} , ascribed to spinel phase, was found. It can be concluded that takovite-like anionic clays are decomposed between 300–400°C to form NiO-like mixed oxide, probably accompanied by trace amounts of spinel-like phases, but a marked crystallization of spinel is observed at higher temperatures above 800°C.

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Smectites from Ziryanovskoe deposit (Kurgan Region, Russia): Relation between composition, structure and technological properties

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This work was carried out to optimize technological processing of bentonites from Ziryanovskoe deposit, situated in the Kurgan region on south-eastern part of the Eastern-Siberia lowland. Recently this deposit is actively exploited. Clays from it are used for drilling fluids, foundry sands and iron-ore pellets.

For investigation of relation between composition and structure of smectites and technological properties of bentonites the following methods were used: X-Ray diffraction, thermal analysis, IR-spectroscopy, EMR-spectroscopy. Technological properties were tested by specification API 13A and VGD-69. The XRD patterns were collected from oriented preparations of natural in air-dried and ethylene glycol-solvated states and after 100, 300 and 550°C heating and from activated samples (2, 3 and 4% of Na₂CO₃) in air-dried and ethylene glycol-solvated states. XRD patterns calculation and spectrum analysis were used for smectites structure study.

Bentonites can be subdivided into brown-grey (I), brown (II) and yellow (III) clays. Among non-clay minerals quartz and feldspars were registered in extrinsic quantities (<5%). The main components are ferriferous, poorly ordered montmorillonites. Predominant interlayer cations are Ca-Mg, but Na-K cations are also present. Content of montmorillonite is about 65-75%. Complicated composition of cations content is confirmed by thermal data and results of exchange capacity study. In addition to montmorillonite, illite and kaolinite are present in small amounts. Content of FeO oxide is varying from, 8.6% in type I clays to 6.9% – in clays of type III by the XRF analysis. Date of

IR-spectroscopy testify to increase structure Fe³⁺ in yellow bentonites. Also, mixed layers kaolinite-smectite was found in this type. Destruction of smectites structure starts during 300°C heating caused by octahedral Fe oxidation.

All investigated bentonites have good rheological behaviour and quality of suspension in activated state, but they have not enough thermal stability. Temperature of second endoeffect is about 510-530°C. Only bentonites of I group have a small effect at 675°C. Smectites of group III have lowest order but they have the best quality of suspension. Processes of Ca-Na replacement take place faster than in I and II bentonites. The best technological properties reach under 2% of soda. Activation in brown-grey and brown bentonites happens in other way. In the beginning (at 2-3% of soda) disordered is increased. Then, in the moment of Ca-Na replacement maximum, ordering increasing is observed. The subsequent activation results in decrease of structure and technological properties.

So, activation of smectites from Ziryanovskoe deposit considerably improves their technological properties. Ca-Na replacement is going faster in smectite which have more disordered structure. At the moment of maximum of replacement smectite have the best ordering and technological properties. Fe in octahedral position decrease thermal stability but increase quality of suspension.

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The possibility of the isotopic dating stages of postsedimentary transformations of clayey terrigenous deposits in the different geodynamical situations

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The paper deals with K–Ar and Rb–Sr isotopic data in the clayey rocks from Vendian of the Russian Platform, Jurassic of the Greater Caucasus and Neogene of the Taman peninsula.

Geodynamic regime and degree of transformation of the investigated sediments is different. The Vendian clays were accumulated and transformed within platform environment. The Jurassic argillites and clayey schists of the Greater Caucasus were folded. The clays of Neogene of the Taman peninsula are low-lithified rocks of the passive continental margins.

The Vendian clay deposits of the Russian Platform were lifted and eroded in Early Cambrian and later, in Early Devonian time. The studied samples were taken from the boreholes: Gavrilov Yam, Soligalitch, Nevel, Kepina. The Rb–Sr isotopic systems of samples from all boreholes show age of 600 ± 50 Ma in the lower part of the profile and 380 ± 40 Ma in the upper part. The age of 380 ± 40 Ma corresponds to the beginning of Hercynian transformation of platform sediments. The K–Ar dating of the same samples lies between 900 and 600 Ma. Increase of K from 2 to 4.5% was accompanied by reduction of the calculated age from 900 to 600 Ma. This correlation is typical for the first phase of diagenetic changes and illitisation of rocks (VINOGRADOV et al., 2003). The age about 600 Ma fix the first post-sedimentary event.

The three profiles of the Jurassic deposits of the Greater Caucasus were studied (along the Terek, the Belaya and the Avarskoe Koysu Rivers). In all studied samples there is a positive correlation between degree of the transformation of clay minerals and changes of calculated K–Ar age. The transformation of the clay minerals increases from north to south along the profiles.

K–Ar and Rb–Sr isotopic systems of the profile Terek demonstrate the age 50 Ma, which reflects an Eocene tectonic phase in the Caucasus and other areas of the Mediterranean foldbelt. But in the southern part of profile K–Ar age of the secondary deformation textures falls to 20 Ma. In the northern part where the clayey rocks were transformed

to a lower grade they keep the age of the structural reconstruction of the Greater Caucasus, about 180 Ma (BUJAKAITE et al., 2003).

Belaya profile shows the least transformation. K–Ar systems indicate the only phase of structural reconstruction of the Greater Caucasus in the Middle Jurassic – 180 ± 15 Ma (KUSHCHEVA et al., 2006). In K–Ar data (the profile Avarskoe Koysu, 165–260 Ma) we can distinguish two groups. The first associates with Early–Middle Jurassic. They are close to stratigraphic age alike the data of the profile Belaya. The second group from the northern part gives the age 240–260 Ma. They correspond to the age of the source rocks. So these isotopic systems manifest Early Jurassic age, the beginning of structural reconstruction of the Greater Caucasus.

The clayey Neogene deposits of the Taman peninsula were studied along the line: Cape Tuzla, Zhelezni Rog, Popov Kamen. The whole-rocks samples from all the sections demonstrate K–Ar ages from ~90 to ~260 Ma. K–Ar age of samples from the ash beds within the clay deposits is 8–10, 11 and 13 Ma. We are sure that the process of the rejuvenation of the K–Ar ages is connected with the post-sedimentary redistribution of material. Thin section observations and investigation of the chemical composition of the samples proves our observation.

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Evolution of swelling and hydration properties of a compacted hectorite percolated by nickel solutions

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Nowadays, subsurface waste disposal is based on the concept of compacted clay barriers, characterized by a low permeability and high cation retention. The aim of this experimental study is not only to reproduce at the laboratory scale the in-situ compaction of saturated clays, but also to focus on the evolution of the clay properties. Therefore, percolation experiments have been performed using an oedometer cell equipped with an injection system under constant pressure (JULLIEN et al., 2002).

The chosen clay is the hectorite from Hector (California, USA), with the structural formula $(\text{Na}_{0.25}\text{Ca}_{0.04})(\text{Mg}_{2.74}\text{Li}_{0.31})\text{Si}_{3.97}\text{O}_{10}(\text{OH},\text{F})_2 \cdot n\text{H}_2\text{O}$. This hectorite is associated with minor calcite. For all experiments, the hectorite sample was compacted at 0.5 MPa, and then soaked at 0.3 MPa with deionised water or $\text{Ni}(\text{NO}_3)_2$ 0.01 M solution. Some mechanical unloadings were also performed along the experiments, in order to test the swelling behaviour of the clay at different exchange rates. Axial strain variations were monitored during testing. Moreover, output solutions from the oedometer, i.e. leachates, have been regularly analysed for Ni^{2+} , Na^+ , K^+ , Ca^{2+} , Mg^{2+} and Li^+ . These analyses allowed to calculate the exchange ratio, K_{Na^+} , defined as the fraction of Na^+ released to the solution, compared to the bulk Na^+ content in the starting clay, in atomic proportion. Two samples, run in the oedometer with $\text{Ni}(\text{NO}_3)_2$ solution, were also obtained, during 180 and 230 days, with an exchange ratio K_{Na^+} of 0.19 and 0.32, respectively. Whatever the run duration, neither Ni^{2+} nor Li^+ have been detected in the leachates, and the Na^+ content in the solutions is around 100 times higher than Ca^{2+} , Mg^{2+} and K^+ . Ni^{2+} has been totally fixed by hectorite and exchanged to Na^+ . Hydraulic conductivity, k , was calculated from the Darcy law, using the expression elaborated for a saturated medium: $k=Q/iS$, with Q the measured volume flow ($\text{m}^3 \cdot \text{s}^{-1}$), i the hydraulic gradient and S the section area of the oedometer (m^2). The obtained hydraulic conductivity k of the compacted hectorite drops in the same range, $4.2 \cdot 10^{-13} \text{ m} \cdot \text{s}^{-1}$ to $4.9 \cdot 10^{-13} \text{ m} \cdot \text{s}^{-1}$, when soaked with water or Ni^{2+} solution, respectively. Swelling strain values determined at the permanent regime are similar: 28% with water and 23% with $\text{Ni}(\text{NO}_3)_2$ solution.

A mechanical unloading after 45 days of experiment with pure water shows that the equilibrium is already reached, since the swelling strain is 44%, identical to that obtained after 180 days. Similarly, the Ni^{2+} exchanged hectorite with $K_{\text{Na}^+}=0.19$ exhibits a swelling strain of 38% after unloading. By contrast, the swelling strain of the same hectorite with $K_{\text{Na}^+}=0.32$ stands to the same value, 23%. These results highlight that the swelling ability of hectorite has been significantly reduced by the $\text{Na}^+ - \text{Ni}^{2+}$ exchange.

The microstructural evolution of hectorite has also been investigated, in order to better understand the influence of nickel on macroscopic properties. For this purpose, a diffractometer equipped with a controlled atmosphere cell was used. The three hectorite samples (soaked with water, soaked with Ni^{2+} solution with $K_{\text{Na}^+}=0.19$ or $K_{\text{Na}^+}=0.32$, respectively) have undergone the same treatments: on the one hand, a thermal cycle (50°C, 100°C, 150°C), and on the other hand, anhydration cycle (relative humidity at 50%, 70%, 80%, 90%, with a constant temperature of 30°C). When increasing temperature, dehydration of interlayer space is delayed when Na^+ is exchanged by Ni^{2+} . Indeed, $d(001)$ reaches 10 Å since 100°C for hectorite soaked with water, whereas the same value is obtained at 150°C for hectorite with $K_{\text{Na}^+}=0.32$. Besides, when increasing relative humidity, hectorite with $K_{\text{Na}^+}=0.32$ swells less than both other samples.

When increasing the interaction with nickel solution, the macroscopic behaviour of hectorite, a smectite known for its swelling properties, is getting close to that of a non-expansive clay. Moreover, nickel has significantly changed hydration properties of hectorite layers. So, evolution of swelling properties at a macroscopic scale can be linked to evolution of hydration properties at a nanoscopic scale.

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Fe³⁺ intercalation into vermiculite or deposition of iron oxyhydroxides? A Mössbauer spectroscopic investigation

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The electron mediator and catalytic properties of intercalated Fe³⁺ in the interlayer space of clays is of general interest. The investigation on which we will report here uses vermiculites from Santa Olalla and Ojén, Spain. As a first step we studied the iron uptake of these by XRD and Mössbauer spectroscopy. As reported in the literature, ion exchange has usually been studied using 1M aqueous solutions of FeCl₃. Such solutions have a pH of about 2, at which some acid attack on the clays may occur. Despite this low pH, the dominating species in the solution will be the oxo-bridged dimer hydrate cation [(H₂O)₄Fe-O₂-Fe(H₂O)₄]⁴⁺. Thus it is this species that is expected to be intercalated rather than isolated hydrated Fe³⁺ ions.

In our first experiments we therefore used lower FeCl₃ concentrations (0.02 M, 0.002 M; total amount of Fe in solution 1CEC up to 10 CEC) to reduce the problem of acid attack. However, even these solutions show a pH of 2.6 which decreases further during the treatment of the clays. Only freshly prepared solutions have been used, since solutions stored for more than a day show some iron oxyhydroxide precipitation.

After treatment at room temperature, the relative intensity of the Fe²⁺ component in the room temperature Mössbauer spectra is strongly reduced compared to the starting vermiculites, while the total Fe³⁺ content has roughly doubled. The average quadrupole splitting of the Fe³⁺ component is lower than in the untreated vermiculite (0.89 mm/s instead of 1.06 mm/s). In fact, the Fe³⁺ component, which can be represented by a single Gaussian distribution of electric quadrupole splittings in the starting material, is better represented by two Fe³⁺ quadrupole doublets in the ion exchanged samples. The splitting of one of these doublets is practically that of the doublet in the original vermiculites, while the other one shows a quadrupole splitting of about 0.6 mm/s. At 4.2 K the Mössbauer spectra of the intercalated samples exhibit a sextet that is quite similar to that observed for ferrihydrite. Such a sextet is always observed independent of the Fe concentration in the intercalating solution. Only its intensity varies with concentration, the lowest intensity being observed for solutions with total iron contents of the order of the CEC. Thus, the most probable interpretation of this result is that an Fe-oxyhydroxide is deposited on the outer surface of the vermiculite particles. This may be due to the formation of positively charged oxidic iron nuclei which interact strongly with the negatively charged clay surfaces.

If one tries to avoid iron oxyhydroxide deposition by insertion of positively charged polynuclear iron clusters like the acetate trimers, one also finds iron oxyhydroxide, although in a smaller amount. This indicates that the acetate trimers get destroyed on the vermiculite surface before they can be intercalated.

The described problems may be due to the complex hydrolysis behaviour of Fe³⁺ ions in aqueous solution and the formation of various iron oxyhydroxides in the pH range below 7. We therefore tried to intercalate Fe³⁺ from of a methanol solution of FeCl₃ according to LETAÏEF et al. (2005). The layer spacing of the intercalated and dried specimen obtained in this way amounts to 13.8 Å in agreement with LETAÏEF et al. (2005). The room temperature Mössbauer spectra look very similar to the spectra of the samples obtained with aqueous solutions, but the Fe²⁺ content is higher than in the aqueous case. However, spectra taken at 4.2 K look quite different. Now there is no sextet due to a magnetically ordered phase. The spectrum looks quite similar to that of the starting material.

This result shows that intercalated Fe³⁺ cannot induce magnetic ordering and the absence of a magnetically ordered phase confirms our earlier conclusion that the magnetically ordered phase observed at 4.2 K in samples prepared in aqueous solution is due to precipitates formed on the external surfaces of the vermiculites. Thus it appears to be impossible to prepare iron intercalation compounds in an aqueous solution because this always results in a simultaneous deposition of an oxyhydroxide. This conclusion also seems to be valid for similar reactions in smectites and all trials of intercalating Fe pillars will face the same problem.

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Point of zero charge and surface acidity constants of $\text{Fe}(\text{OH})_2$

Diana LIEBER and Helge STANJEK

Green Rust (GR), a group of Fe(II)–Fe(III) layered double hydroxysalts, is a prevalent phase generated by steel corrosion (ABDELMOULA et al., 1996). To predict the retardation behaviour of actinides by GR, it is important to investigate ferrous hydroxide, $\text{Fe}(\text{OH})_2$, as well, for it is known to be a common precursor in the formation of GR and has a similar structure (GENIN, 2004). Presumably, elements adsorbed onto ferrous hydroxide might easier get incorporated into GR.

Adsorption of ions and molecules on a mineral surface depends on the charge of both. The ability of a substance to develop a certain surface charge as a function of pH is characterized by the point of zero charge (PZC) and the surface acidity constants. YOON et al. (1979) proposed an approach to calculate these values from crystallographic data for various minerals. With that, they estimated a pH_{PZC} of 11.87 for ferrous hydroxide.

For testing this value in the present work the PZC of ferrous hydroxide is determined experimentally via potentiometric titration. To prevent oxidation of ferrous iron, experiments are conducted in a multibatch setup strictly closed to air. Synthesis of ferrous hydroxide and titration are conducted in one step: by using bases of different concentration in the synthesis of ferrous hydroxide the amount

of excess protons and hydroxyl ions respectively is varied. Remaining ions represent the background electrolyte. After equilibration the difference between the measured pH in the solution and the pH calculated from the surplus of hydroxyl ions after synthesis is determined. Subsequently, the surface acidity constants are calculated by modelling the titration data with the computer program FITEQL (HERBELIN & WESTALL, 1999).

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Mineralogical signatures of weathered Late Holocene ash layer from the island Mljet in Croatia

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Mljet is the southeasternmost pearl of the Croatian archipelago. Due to the prevailing Mesozoic carbonate rocks exposed at the surface, the morphology of the island is characterized by deep dolines and karst valleys. These karstic forms retain fresh water forming shallow lakes (blata) in the NW part of the island. In the SE part, these depressions may be filled by thick aeolian deposits of fine- to medium-grained sand, which was commercially exploited in the past. The Pinjevica pit is the largest excavation on the island, containing estimated amount of 1.4 mega tons of quartz-dominated sand interlayered by 35–40 cm thick vitric tephra (KRKALO & PENCINGER, 1995). The tephra layer is slightly lithified and marked by up to 1 cm wide bioturbation channels with loose sandy infillings. The sands are interpreted as distal Late Würm fluvial deposits that were recurrently transported by wind to the recent position (BOGNAR et al., 1992).

Samples were scraped off from the tephra layer in three equal intervals to represent the entire layer. The aliquots were wet sieved and fractions <32 µm was separated from several larger grain fractions which were separated to heavy and light fractions. In all samples the <32 µm fraction makes around 98 wt% of the bulk sample. The XRPD analyze of the air dried, etilenglycole saturated and heated <32 µm fraction revealed only XRD “amorphous” phase(s). Due to the absence of carbon and volcanic glass in the samples, the phase(s) may be recognized as non-crystalline to poorly-ordered clay mineral(s), allophane and/or imogolite. Allophane and imogolite are indicative for early-stage weathering product of vitric volcanic ash in highly moist or wet systems with good drainage (WADA, 1989) suggesting that similar climatic and pedogenetic conditions were already established in Pinjevica at the time of tephra deposition.

Altered tephra can be correlated to coeval distal lavas by their crystalloclastic mineral chemistry. The grain morphology and chemical composition of residual minerals from the analysed tephra allow us to distinguish the volcanic crystalloclasts [sanidine ($\text{Or}_{51.5-86.4}\text{Ab}_{11.7-45.2}\text{An}_{0.8-5.6}$), plagioclase ($\text{Or}_{5.1-9.4}\text{Ab}_{38.6-53.2}\text{An}_{38.0-56.2}$), biotite ($\text{Mg\#}=57.4-63.4$; $\text{TiO}_2=4.4-4.8$ wt.%), clinopyroxene ($\text{Di}_{46.9-49.4}\text{En}_{34.7-38.6}\text{Fs}_{13.1-17.9}$), orthopyroxene ($\text{Di}_{1.6-2.4}\text{En}_{59.6-63.2}\text{Fs}_{35.3-38.8}$) and Ti-magnetite (8.7 wt.% TiO_2)] from the aeolian crystalloclasts (quartz>spinel, diopside/augite, enstatite, actinolite, pumpellyite, epidote, adularia, albite). Spinel composition ($\text{Mg\#}=32.5-64.0$, $\text{Cr\#}=0.40-0.84$) is similar

to the spinels from the sandstones of Upper Cretaceous to Late Eocene flysch basins located around 450 km to the NW (LENAZ et al., 2000) and from the matrix of Upper Jurassic mélangé from the Dinaride Ophiolite Belt in the central Bosnia (MIKES, unpublished). These findings confirm flysch as potential source of Pinjevica sands as it was constrained by BOGNAR et al. (1992).

In the adjacent Saprunara Bay a well developed “pedologic complex” shows onset of soil formation from 3.776–3.363 ka BC to around 3.115 ka BP as may be inferred from the ¹⁴C corrected age on Gastropod shells at the bottom of the complex (BOGNAR et al., 1992) and from the predominance of arboreal pollen, particularly of Pinus which is supposed to have been introduced on Mljet by Greek or Roman settlers (JAHNS & VAN DEN BOGAARD, 1998). Since the soil formation interferes with the deposition of analysed tephra, we search for the south Italian volcanoes erupted between around 5.8 and 3.0 ka BP with NE dispersed tephra. The recurrent eruptions from the Campi Flegrei caldera in the period from 4.800 to 3.800 ka BP with the highest magnitude eruption of Agnano–Monte Spina (AMS) dated to 4.100 ka BP (DE VITA et al., 1999) are the best source candidate of the Pinjevica tephra. However, abundant volcanic plagioclase and orthopyroxene which are not related to the AMS tephra signalize an another still unidentified source.

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Geological prospecting of kaolin and kaolinite clays deposits on territory of the Western Carpathians (Slovakia)

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The main phase of kaolinization in the Western Carpathians (Slovakia) took time from Badenian to Pontian. We distinguished primary (weathering and hydrothermal) and secondary (sedimentary) genetic types of kaolin deposits in the Western Carpathians. The weathering genetic type is mainly the result of alteration of different type of metamorphites and granitoids. The sedimentary deposits are represented by kaolin silts, sands and gravels. They are usually formed by redeposition of the primary weathering crust on the short distance. We also recognise kaolinite clays depos-

it which formed by redeposition of the primary weathering crust on the longer distance. Surveying and prospecting of kaolin and kaolinite clays deposits is quite difficult on the territory of the Western Carpathians. This is the reason why we suggested simple prospecting criteria for geological survey. The most important prospecting criteria are: (1) Geological position, (2) Mineral composition; (3) Intensity of alteration; (4) Palaeoclimatic; (5) Technological; and (6) Commercial (economic).

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Mössbauer spectroscopy investigation of ground and acid treated vermicullite

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Grinding of vermicullite results in particle size reduction (delamination and lateral size reduction), folding and gliding of layers and aggregation of the newly formed particles. Additionally, grinding also produces rearrangement of the coordination polyhedra and diffusion of atoms (mainly protons “prototropy”) within the structure, yielding after progressive grinding amorphous materials. These effects produce surface modification of the mineral favouring the acid attack.

The acid treatment of an unground sample leaches partially magnesium and iron from the octahedral layer of the vermicullite lattice. Increasing the acid concentration up to 1M a remarkable decrease of magnesium, aluminium and iron occurs accompanied with an increase of the silicium content in the residual solid. Nevertheless, vermicullite still remains after the acid attack with the highest acid concentration used in this work (1M, at 80°C during 24 hours). Grinding (with vibratory mill) favours the attack of the samples, but the iron content of the residue increases after the acid treatment. Vermicullite ground for 4 minutes keeps its structure after acid attack with 0.25 M and 0.5 M HCl. However, treatment with 1M HCl results in an amorphous silica with a very high surface area ($S_{\text{BET}} = 720.26 \text{ m}^2\text{g}^{-1}$). It is coloured yellow due to deposition of an iron oxide-hydroxide which is very probably akaganeite according to XRD.

To get more insight in the fate of iron species in the solid we undertook a Mössbauer investigation of the ground and acid treated solids. The spectra of the starting material can be interpreted by the superposition of three quadrupole doublets assigns to one octahedral Fe^{3+} and two Fe^{2+} sites. After grinding for 4 minutes the Mössbauer spectra keep the normal features and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio remains

almost unchanged although the XRD data show severe attack on the structure of the vermicullite. That means that the particle size and the long range order suffers strongly from grinding whereas the local ordering is not strongly affected. Just a slight line broadening of the spectra indicates some alteration of the mineral.

During treatment of the unground vermicullite (7.50% iron as Fe_2O_3) with 1M HCl almost half of the iron is lost to the solution. The Mössbauer spectrum is still very similar to the typical spectra of vermicullites, but there is a slight decrease of the Fe^{2+} content. The decrease of the quadrupole splitting of Fe^{3+} site indicates a superposition of the vermicullite Fe^{3+} site with some other Fe^{3+} sites of lower quadrupole splitting due to the presence of an $\text{Fe}-\text{O}-(\text{OH})$. The sample ground for 4 minutes and treated with 0.25 M HCl shows still the typical vermicullite Mössbauer spectrum with a $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio similar to the untreated sample. The samples ground for 2 or 4 minutes and treated with 1M HCl solution are completely orange and according to the Mössbauer spectra only Fe^{3+} remains. Its quadrupole splitting dropped to about 0.6 mm/s indicative for Fe-oxyhydroxides. Spectra of these samples taken at 4.2 K show the magnetic hyperfine splitting of akaganeite.

Oxidation of the structural iron in the vermicullite, which has been considered as an essential step during grinding since the vibratory mill is very energetic, does not occur in our sample according to the Mössbauer results. The acid attack leads to dissolution of iron, but some Fe^{2+} and Fe^{3+} remains in the structurally damaged vermicullite. The vermicullite is completely destroyed only after an acid attack with the highest acid concentration applied and only akaganeite precipitates on the amorphous SiO_2 .

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Particularities of Mössbauer spectroscopy for the archaeological potsherds dating

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The possibility of Mössbauer spectroscopy for dating of the ancient pottery based on the evaluation of absorbed dose has been demonstrated (EISSA et al., 1979). The linear dependency estimated (EISSA et al., 1979) between the relative intensity of peaks corresponding to Fe(III) and the dose absorbed by sample was confirmed also (AMULEVICHIOUS et al., 1989).

Number of potsherds excavated on the territory of historical memorials of Hanty–Mansi national district were studied. We have used both a discrete spectrum description and P(Qs) quadrupole distribution restoration method. The principal particularity of any observed spectra is the presence of at least four nonmagnetic components: two doublets associated with Fe(II) and two doublets associated with Fe(III). Mutual overlapping of left peaks of all Fe(III) and Fe(II) doublets occurred. This greatly influences upon the parameter informative for dating – relative intensity of Fe(III) doublet peaks. The nature of each of the spectrum

components is estimated, that allows us also to make some suggestions concerned on pottery production technology.

Alternative parameter received from spectrum fitting which characterized the dose absorbed by potsherd is offered – a relative degree (RD) of overlapping for Fe(III) quadrupole components peaks.

Dating of 10 archaeological potsherds has been performed by means of building “RD vs. absorbed dose” dependencies. Received results are in good agreement with radiocarbon data.

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Characterization of changes of low and high ordered kaolinite after bioleaching

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Two samples of well and poorly ordered kaolinite samples KG1 and KG2 (designated according to the Handbook for Clay Minerals) were studied with the aim to describe their structural changes after biological removal of iron ions. As follows from the paper of MAURICE et al. (2001) the using of iron and silicate reducing microorganisms has an important influence on the dissolution rates of kaolinite mineral.

The kaolinite samples were inoculated with mixture of *Bacillus cereus* and *Bacillus purilus*, originally isolated from the kaolin deposits in Lučenecká Kotlina in Slovakia. The active role of bacteria on the kaolinite was investigated and the process of elements Fe, Al and Si dissolution monitored during 100 days lasting incubation. The changes in chemical composition, particle size distribution, structure of minerals, adsorption properties and pore size distribution of the solid residua were evaluated in order to emphasize the influence of the degree of disordering in samples.

The results after a 100-days experiment show that in spite of almost equal contents of Al and Si in both samples KG1 and KG2, only the extractions of Al are comparable. The extractions of Si and Fe from the poorly ordered kaolinite sample KG2 are higher than from the well ordered KG1 (Table 1). This indicates that the higher disorder facilitates the role of bacteria in selective dissolution of kaolinite mineral.

Other changes were identified from the adsorption-desorption isotherms. The shape of the isotherms in case of well ordered structure of kaolinite sample KG1 is more typical for nonporous materials. Comparing them in the range of relative pressure 0.8–0.99, the higher uptake in the

amount of nitrogen was observed at the low ordered kaolinite sample KG2 after biological activation and the narrow hysteresis loop indicates the presence of mesopores and macropores. Parameters determined from the adsorption measurements describe the specific surface area S_{BET} as well as the total pore volume V_0 of samples prior and after bioleaching. The values of specific surface area very slightly decrease after bioleaching, explaining that no new surfaces were formed during the process. Moreover, an effect of aggregation may be also present. In contrary to that, the total pore volume increases indicating changes in the structure of mineral after bio-activation.

As follows from Figs. 1 & 2, the distribution of pores for highly disordered sample is quite different in comparison to the well ordered sample KG1. The dissolution of impurities from KG2 makes more pores, meso- and macro- accessible for nitrogen molecules. It can be concluded that the bioleaching of iron ions from samples of kaolinite with different degree of disorder is more effective in case of more disordered structure.

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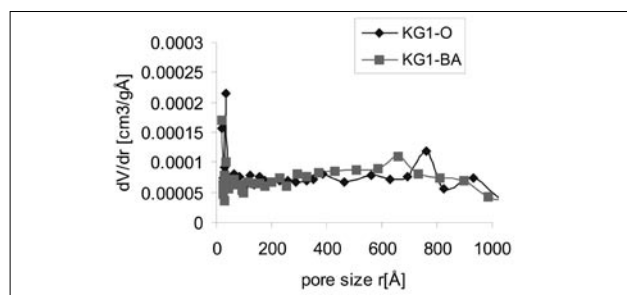


Fig. 1 Pore size distribution for the sample KG1.

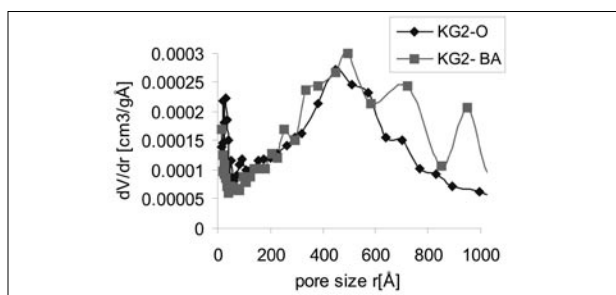


Fig. 2 Pore size distribution for the sample KG2.

Extraction of elements [%]	KG1–bacterially activated	KG2–bacterially activated
Si	0.95	2.21
Fe	8.24	12.04
Al	1.6	1.7

Table 1 Extraction of Si, Al and Fe from kaolinite samples KG1 and KG2.

Intercalation of aniline in Wyoming montmorillonite exchanged with different cations

Fabrice MULLER, Jean Michel BÉNY and Mathieu GAUTIER

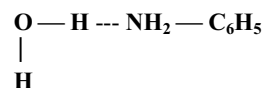
Intercalation and deintercalation of organic molecules in the interlayer space of phyllosilicates represent an important interest in the development of new materials with desirable properties (catalysts, sorbents, ...) and in environmental protection and rehabilitation (waste deposits, polluted soils, ...). In this work, we turn one's attention to the interaction of aniline with montmorillonite. Firstly, because this compound serves as a model for the sorption of aromatic amines by expanding layer silicates, and secondly, because aniline is a very dangerous polluting molecule.

The interaction of aniline with SWy2 Wyoming montmorillonite (structural formula: $(\text{Na}_{0.14}\text{Ca}_{0.05}\text{K}_{0.01})(\text{Al}_{1.56}\text{Fe}_{0.21}\text{Mg}_{0.23})(\text{Si}_{3.95}\text{Al}_{0.05})\text{O}_{10}(\text{OH}_2 \cdot n\text{H}_2\text{O})$ exchanged with different interlayer cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} and NH_4^+) is obtained by placing the sample in aniline vapour. Mass measurements of the sample versus time show that saturation of adsorption process is obtained after 16 hours of exposure.

Carbon and nitrogen were quantified after interaction with a LECO CNS-2000 analyser. The results confirm that aniline molecules are adsorbed. The quantity of adsorbed molecules is more important than the CEC (Cationic Exchange Capacity) of the sample. For example, for 100g of Na-SWy2, 0.088 mole of aniline are adsorbed after 16 hours of exposure, while the CEC value equals to 0.065 mole/100 g. The interlayer cation type influences the amount of aniline taken up by clay. For Mg^{2+} and Ba^{2+} cations, the proportion of adsorbed aniline is approximately equal to 4CEC, whereas this value is lower with Na^+ ($\cong 1.5\text{CEC}$) and NH_4^+ (2.5CEC).

Characteristics of the absorption (localisation of aniline molecules, type of bonding between layer and molecule) have been studied using infra-red spectroscopy. The comparison between the original material spectra, intercalated with aniline montmorillonite spectra and liquid state

aniline spectra shows that all the characteristic bands of aniline are found in the intercalated with aniline montmorillonite spectra. The N-H stretching wavenumbers are lower for the aniline-montmorillonite complex than for the dilute state (or like gas state) aniline (3388 cm^{-1} and $3312\text{--}3324\text{ cm}^{-1}$ for the aniline-montmorillonite complex; 3480 cm^{-1} and 3395 cm^{-1} for the dilute state); this implies an increase of the N-H bonds length in the complex because of a strong hydrogen bridge formation between aniline and water molecule. Aniline anchorage seems to require the presence of interlayer water.



The C-N band wavenumber shifts from about 1275 cm^{-1} in the liquid state or dilute state to 1250 cm^{-1} in the complex which proves a length increase for this bond in the complex consistent with the strong hydrogen bridge formation.

The structural changes have also been investigated. For this purpose, a diffractometer equipped with a controlled atmosphere cell was used. The patterns have been recorded with the relative humidity of 50% at 30°C . For Na and NH_4 -samples an increase of $\cong 0.3\text{ nm}$ in the d -value of the 001 reflection after aniline treatment confirms clearly the fixation of the molecule in the interlayer space of the montmorillonite. A systematic decrease of the width at mid height is observed for the adsorbed samples indicating a better stacking of the layers which can be attributed to a structural reorganisation of the interlayer space. For all of studied samples, the basal spacing after the adsorption is $\cong 1.5\text{ nm}$. This result is compatible with an orientation in which the plane of the benzene ring is practically perpendicular to the silicate surface of the sample.

Structure and dynamics of cationic surfactants intercalated in synthetic clays

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Polymers are commonly admixed with a variety of both natural and synthetic compounds to improve their performance. Nanocomposites constitute a new class of materials with an inorganic ultrafine phase dispersion (e.g. clay minerals) of the order of a few nanometers that endows them with unique properties not shared by conventional materials and offer new technological and economic opportunities. To obtain clay-polymer nanocomposites, one of the critical steps is the surface treatment of the mineral. Cationic surfactants are ion-exchanged with interlamellar cations to form intercalated clay-surfactant hybrids.

The lamellar structure of clays, also named phyllosilicates, consists of layers formed by condensation of sheets of linked $\text{Si}(\text{O},\text{OH})_4$ tetrahedra with those of linked $\text{M}_{2,3}(\text{OH})_6$ octahedra, where M is either a divalent or a trivalent cation. Three-sheet clays result from 2:1 condensation, the octahedral layer being sandwiched between two tetrahedral layers. Trioctahedral clays show their three trioctahedral sites occupied by Mg(II), dioctahedral phyllosilicates have two of three octahedral sites filled with Al(III). Clay platelets are negatively charged, as a result of cation isomorphous substitution either in the octahedral layer or in the tetrahedral layer. Exchangeable cations such as sodium occupy the interlamellar space in order to preserve electroneutrality.

Three series of intercalated clay minerals with gradually decreasing layer charge (0.75–0.30 $e/\text{O}_{10}(\text{OH})_2$) were prepared from synthetic Na-saponites (trioctahedral clay

mineral) and Na-laponite (dioctahedral clay mineral), using hexadecyltrimethylammonium (HDTA) bromide, (2-hydroxyethyl) dimethylhexadecylammonium iodide (HEDMHA) and di-(2-hydroxyethyl) methylhexadecylammonium iodide (DHEMHA). The content of the organic phase in the cation exchanged-clay was determined from the weight loss of the decomposition of the remaining alkylammonium cations in the clay mineral by means of thermogravimetric analysis. The degree of the cation exchange was calculated as a ratio between the organic content and CEC of clay.

¹³C CP MAS NMR studies provided the structural and dynamic information at the molecular level such as the gauche/trans conformational ratio and interaction sites between the surfactant and the silicate layer. The results have shown that amount of the all-trans conformation decreases progressively as the saponite charge grows up to 0.60, and the hydroxyethyl chain influences the long chain conformation, and hydrogen bonding between the hydroxyl group of the surfactant and oxygen atoms of the silicate layer could increase surfactant anchoring, favouring alkyl chain packing and the all-trans conformer. The XRD analysis and FTIR spectroscopy appended these results. The less densely packed gauche conformation leads to the increase of the interlayer distance, and the charge size and its location effect the surfactant intercalation and the trans conformer number.

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Dating of fault clays of the North Anatolian Fault Zone, Turkey

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The North Anatolian Fault Zone (NAFZ) is one of the main active tectonic structures of the world which defines the border between the Anatolian block and Eurasian plate. Although the age of the fault zone is under discussion, it is agreed by previous works (based on relative dating) that the initiation age of the NAFZ is mid or late Miocene (BARKA et al., 2000; BOZKURT, 2001; ŞENGÖR et al., 2005). This study is the first attempt to provide new geochronological data on the NAFZ on the basis of age dating (K–Ar) and stable isotope (¹⁸O/¹⁶O) tracing of illite and other authigenic minerals (in various clay size fractions between <0.2 to >4 µm) formed during the near surface faulting. It was determined from the mineralogical studies that fault gouge samples are completely altered as pseudotachylytes and that authigenic minerals such as illite, smectite, kaolinite, mixed layered illite/smectite and chlorite are generally found in fine grained size.

Among the clay-rich fault gouges collected along the NAFZ, only four samples were suitable for authigenic illite development and dating. Illite samples from Gerece and Mudurnu in western section of the NAFZ yielded K–Ar ages of 56.5 and 58.7 Ma, respectively. On the contrary, the ages obtained from Koyulhisar and Resadiye areas from eastern part of the fault zone are younger and they yielded ages of 34.5 and 26.6 Ma, respectively. The old ages are believed to be heritage from strike-slip faults developed

following the collision of the African plate with Anatolia. The variation in old ages could indicate that margins of the Neotethyan Ocean were irregular before the collision. A relatively younger age from the Resadiye area might indicate that the initiation age of the NAFZ is as old as 26.6 Ma which is nearly consistent with the age of collision between Anatolian block and Arabian plate in southeastern Turkey (ŞENGÖR et al., 1979; ŞENGÖR & YILMAZ, 1981). However, further dating is needed to obtain a precise age for the commencement of the NAFZ.

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Preparation of noble metal bentonites for catalytic purposes

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Clay rocks are widely used as catalysts in natural as well as chemically treated forms. Different cation exchanged clays are also applied. The cation exchanged forms can be found under natural, geological conditions, so the simultaneous effect of the clay and the cation can be significant for the transformations of organic matter in nature. Noble metals, e.g. silver and palladium, are widely applied as catalysts in different oxidation states: palladium is used for hydrogenation processes and silver is an important catalyst in photochemistry. In this work palladium- and silver-bentonites were prepared and their properties were studied by X-ray fluorescence spectroscopy, X-ray diffraction, thermal analysis, redox potential measurements and scanning electron microscopy.

The sorption of palladium(II) ion was studied on sodium-bentonite. To avoid the hydrolysis of Pd(II) and the acidic destruction of clay, Pd(II) was applied as positively charged $[\text{Pd}(\text{NH}_3)_2]^{2+}$ and $[\text{Pd}(\text{en})_2]^{2+}$ complexes. The X-ray diffraction and thermal analytical studies show that palladium(II) ions are not introduced into the interlayer space of montmorillonite. They are mainly sorbed on the deprotonated silanol sites of the clay rock. The quantity of the sorbed palladium(II) ions is in a fairly good agreement with the concentration of the surface silanol sites. The results of the thermal analysis show that the palladium(II) sorbed on the surface of the clay can be reduced to Pd(0). By this method, applying complex forming agents, palladi-

um catalysts with 2 or 0 oxidation state can be produced. However, the thermal treatment increases the concentration of the amorphous phase in bentonite, which is more desirable from the catalytic point of view.

In the system of silver(I) ion/sodium-bentonite at pH=4 and at low silver concentrations a pure sodium-silver ion exchange process takes place in the interlayer of montmorillonite. Redox potential measurements show similar tendencies to sorption measurements: the experimental data show significant uncertainties when the silver concentration is smaller or equal to the hydrogen ion concentration of the solution. Hydrogen ions participate in a competitive cation exchange process in the clay/solution system. When the concentration of silver ion is low this process cannot be neglected.

Scanning electron microscopic studies show that there are places on both cation exchanged bentonites where the concentration of silver as well as palladium is significantly greater than the average concentration of the ions. These are considered as local metal ion enrichments. Some silver enrichments studied by SEM can be up to 100% of silver content. It shows that the reduction of silver (I) to metallic silver can also take place. Thermoanalytical study of silver-bentonite shows an exothermal reaction at 361°C. It refers to the oxidation of metallic silver, as proved by the change of the silver-bentonite color which is originally dark grey and becomes lighter after the heat treatment.

Nature and alteration of clay minerals in brown forest soil profiles (Luvisols) of Cserhát Mountains (North Hungary)

Tibor NÉMETH and Péter SIPOS

Brown forest soils cover significant proportion of Hungary's area, therefore they are very important from the point of view of the ecosystem, of the environment and of the agriculture. It is well known that the physico-chemical properties of soils depend on their clay mineral composition. Results of earlier studies within the frame of a regional environmental geochemical research project of the Cserhát Mountains in North Hungary confirmed that due to their adsorption capacity clay minerals play an important but variable role in the distribution of trace elements within a soil profile among the different soil horizons (SIPOS et al., 2005a, b). As the adsorption properties of clay minerals are influenced by variable and sensitive parameters such as their layer charge and swelling characteristics, alteration of clay minerals in pedogenic processes affects the distribution of heavy metals in soils. Clay mineralogy findings including the detailed characterization of clay minerals in four brown forest soil profiles developed on different bedrocks, but influenced by similar pedogenic processes (e.g. clay illuviation) and a suggestion on the possible genesis and evolution of clay minerals in Luvisols of the Cserhát Mountains will be presented.

The clay mineral composition of less than 2 μm fraction of 17 soil samples was studied and characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) using the following diagnostic treatments: ethylene glycol and glycerol solvation, Mg- and K saturation, Green-Kelly test, alkyl-ammonium layer charge determination, and analytical electron microscopy for chemical analyses.

Brown forest soils (Luvisols) formed on various parent rocks show differences in the details of their clay mineralogy and consequently are characterized by different clay mineral alteration processes. A common feature in all four studied soil profiles is the predominance of swelling clay minerals. Siltstone bedrock weathered to chlorite/vermiculite and vermiculite in a less developed, shallow soil

profile with considerable calcite content in the BC and C horizons. Soil chlorite or chlorite/vermiculite exhibits only a restricted expansion upon ethylene glycol solvation, does not swell after Mg-saturation and glycerol solvation, and is partially resistant to heat treatment and K-saturation.

The major product of soil formation in a clayey, well developed, deep soil on siltstone parent material is a typical soil smectite with heterogeneous charge distribution between the layers, but originating dominantly from octahedral substitution (montmorillonite). This soil smectite contains considerable amount of iron. Mobilization and accumulation of iron in different oxi-hydroxide forms in the studied soil profiles is a common process. Some conversion of octahedral to tetrahedral charge, and the slight increase of total layer charge in these horizons could be the consequences of pedogenic processes.

The characteristic clay minerals in the soil formed on limestone are smectite and illite/smectite with evident charge reduction and degradation of illite and smectite during the weathering. In this profile the illite/smectite interstratification seems to be the result of a polyphase process, even including reaction pathways with opposite directions.

Dominance of low layer charged smectite (montmorillonite) in the C horizon suggests its formation from feldspars and volcanic glass in a soil developed on andesite parent rock. This smectite alters to high charged vermiculite during pedogenesis in the B and A horizons.

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Clay minerals and selected ecological aspects of soils on the island Veliki Brijun, Croatia

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The archipelago Brijuni is located southwest of Pula, parallel to the peninsula of Istria. Veliki Brijun is the largest and most important island, where the major part of the cultural heritage and the most important new objects are situated. A well equipped arboretum with a costly infrastructure was established in 1987. The basic idea was to give a floristic overview on the Mediterranean flora as well as on trees and shrubs from completely different floristic areas from various countries as examples to document the lively diplomatic activities of the former Yugoslavian President Tito. Due to the war and abandoned care the arboretum is in a bad condition.

An ecological survey was carried out by a diploma student to proof the hypothesis whether the general idea of the initiators of the arboretum is sustainable or whether an improved concept should be developed under the present ecological conditions with less maintenance efforts. Scientific soil research seemed to be a fundamental tool to answer these ecological hypotheses and was meant to support a new concept.

The soils are generally classified as chromic Luvisols. Data on mineralogical, physical, chemical and hydrological soil properties were collected and evaluated in six soil profiles. Their ecological relevance was analyzed and served as an important deciding factor for the presented concept for the arboretum "Putevima Mira".

The arboretum was mapped in various aspects: among the maps one shows the depth of the soils and another one documents the position of a "dense clay-layer".

Mineralogical analyses show illite and kaolinite – poorly crystallized – as the main clay minerals in the soils. Vermiculite and mixed layer minerals are rare; smectite and chlorite couldn't be found. In general the soils show a decrease of illite and an increase of vermiculite in the deeper

part of the profiles caused by illitisation processes on the soil surface.

Solifluction processes are visible in profile 4, which is situated at the coast. It can be seen, that in the past the soil moved from higher parts of the island downwards to the coast. In two profiles (5 and 6) the anthropogenic influence is visible: to improve site quality for exotic plants 30 to 50 cm of a terra rossa soil was deposited onto the existing soil and buried the naturally developed A-horizon.

Technical tests show the high density of the clay layer in a depth of about 50 cm. This dense structure and the low porosity (similar to clay deposits) are unfavorable for "exotic" plants.

Woody species can hardly root in these shallow soils; they penetrate into cracks between limestones filled with fine soil. In general, a sufficient amount of water can be stored in the soils for the adapted Mediterranean vegetation. However, the water potential/water content curves for the Brijuni soil samples proof that the water is retained in the pores of the soil with such a high tension that only a small amount of the water is plant available and allows only woody species adapted to the climatic and pedologic situation to cover their water requirements without extensive care. The additionally heaped-up soil material did not improve the hydrological properties of the soil. Therefore, only trees and shrubs adapted to the respective ecological site conditions should be displayed in the arboretum. If we assume an annual precipitation of about 800 mm and an annual mean temperature of more than 14°C, the water requirements of non indigenous plants cannot be met without additional irrigation. A sustainable concept for the Arboretum "Putevima Mira" should rely on the attractive diversity of Mediterranean woody and herbaceous species.

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Influence of the synthesis conditions on the physico-chemical characteristics of porous clay heterostructures

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Successful synthesis of mesoporous solids from layered clays by GALARNEAU et al. (1995), resulted in the formation of porous clay heterostructures (PCH), and provided link between microporous pillared clays and ordered mesoporous silica-based materials. In the synthesis of a PCH the clay is first opened up by the introduction of a cationic surfactant via an ion exchange reaction, thus allowing easier access to the interlayer region. Subsequently, neutral amine surfactant molecules and the silica source (TEOS) are intercalated into the interlayer region, where the self-assembly of the silica species leads to the formation of a porous network. The final properties of such materials may be influenced by the synthesis conditions (BENJELLOUN et al., 2002).

The aim of this study was to investigate the role of various synthesis parameters in the preparation of porous clay heterostructures derived from natural montmorillonites. Among the studied factors were:

- the origin of clay;
- the carbon chain length of neutral amine;
- the molar ratio of reactants.

The montmorillonite clays used in this study were the sodium form of montmorillonite from Milowice deposit (Poland), and the calcium form of montmorillonite from Jelšovský Potok deposit (Slovakia), referred to as Na-M and Ca-JP, respectively.

In the first step of PCH synthesis, inorganic cations in the interlayer space of Na-M and Ca-JP were exchanged with hexadecyltrimethylammonium cation (HDTMA⁺). The XRD patterns of organoclays HDTMA-M and HDTMA-JP showed an increase of basal spacing d_{001} to 21.2 Å, as compared to parent montmorillonites (12.1 Å for Na-M and 15.1 Å for Ca-JP). This value points to the pseudotri-molecular configuration of alkyl chains in the interlayers of both clays. FTIR spectroscopy also confirmed the presence of organic cations in the smectite structure. Stretching and bending vibrations of CH₃ and CH₂ groups of alkyl chains were observed at 2923 and 2851 cm⁻¹ and 1488 and 1470 cm⁻¹, respectively.

In the second step of synthesis neutral amine (alternatively decylamine or dodecylamine, differing by the length of carbon chain) and TEOS (tetraethylorthosilicate) as silica source were added to organoclay. Two different ratios of organoclay/amine/TEOS were used: 1/10/75 and 1/15/75. XRD analysis showed that intercalation resulted in a significant increase of the basal spacing and both the ratio of reactants and the chain length of the neutral amine influenced the structure of the resulting solids. E.g., in the case of HDTMA-M intercalated with decylamine the d_{001} value increased to 32.8 Å for the ratio 1/10/75 and to 33.2 Å for the ratio 1/15/75. Materials obtained with the use of dodecylamine showed even larger basal spacing of 35.7 and 36.4 Å for the ratio 1/10/75 and 1/15/75, respectively. FTIR spectra of the intercalated solids showed that the major changes were associated with the complex absorption band of Si-O stretching vibrations, whose broadening reflected the hydrolysis of TEOS.

To complete the synthesis the intercalated clays were subjected to calcination in air at 650°C. The absence of any vibrations characteristic of organic groups in the FTIR spectra confirmed that thermal treatment removed completely the organic templates. The materials obtained from Ca-JP showed slightly higher specific surface area, as compared to those prepared from Na-M, e.g. for the solids templated with dodecylamine at the reactant ratio of 1/15/75 the specific surface areas of JP and M-based materials were 810 and 842 m²/g, respectively. Dominant pore radius was 24 Å in both cases.

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Brick kilns of northern Lower Austria: History and geology

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In northern Lower Austria a wide abundance of different clay materials for brick-making is given due to the geological setting. The Hollabrunn district belongs to the Molassezone (Neogene sediments), as well as – with some of its western parts – to the eastern part of the Bohemian Massif (granites). Both tectonic units are covered partly by Quaternary loess and loam.

In total 150 brick kilns and eight clay pits are recorded as operating in the Hollabrunn district during the period 1780–1980 (PAPP et al., 2003). Since the end of the Second World War the brick industry has dramatically changed. The production formerly mainly based on handcraft changed step by step to an almost totally automatic one. As a result of this process nowadays only a single kiln remains in use in the area.

Based on a great variety of historical sources and the distinctive seals impressed by each kiln on the bricks it produced, it was possible to reconstruct the history of almost all the kilns and their ownership.

Considerable attention was paid to the geological setting and the petrographic characteristics of the raw materials used for brick-making in this area.

The Neogene deposits of the Hollabrunn district comprise marine and fluviatile sediments. They are mainly covered by aeolian sediments (loess). Analyses of grain-size distribution, whole rock composition and clay mineralogy were carried out in order to describe the quality of the clay material for brick making. Three different lithostratigraph-

ic formations were found to be most suitable, ranging from Lower Ottnangian to Pleistocene age.

The marine Zellerndorf Formation (Ottangian) is free of carbonate and consists of silty clays to clayey silts. The clay mineral composition dominated by smectite may influence the drying behaviour negatively. Gypsum, pyrite and their weathering products result in increased SO₂-contents during firing.

In the upper part of the Zellerndorf Formation finely laminated diatomites are intercalated, which are used for the production of lightweight insulating bricks.

Today the most important geological formation for brick-production is of Karpatian age. It is represented by pelitic and sandy sediments of the Laa Formation. According to its marine origin the sediments tend to be very homogeneous. Mineralogy and grain-size distribution show little variation over wide distances, an important factor for a constant quality.

From a historical point of view the Pleistocene loess and loamy loess deposits were the most common sediments used for all kinds of bricks. Due to the local geological situation, the mineralogical composition as well as the grain-size distribution show great variability. This is the reason for the rather heterogeneous quality of historical bricks.

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Acid treatment of clay minerals: a FTIR spectroscopic study

Martin PENTRÁK and Jana MADEJOVÁ

Clays are widely used materials in various industrial applications either in their original or in adapted forms. Some properties of clay minerals can be modified, e.g. by acid activation, to increase their efficiency for selected utilization. Inorganic acid treatment causes partial or complete destruction of the clay minerals structure depending on the reaction conditions and on the availability of the interlayer space. During the acid attack the central atoms from the octahedral as well as tetrahedral Al are removed from the clay structure. The final reaction product is a microcrystalline, protonated SiO_2 (MADEJOVA et al., 1998). Acid activation of clays is an effective method for preparation of advanced adsorbents, catalysts or catalyst carriers (ADAMS, 1987; BROWN, 1994).

The aim of this investigation was to follow the changes in the clay minerals structures during treatment in hydrochloric acid. The fine fractions of four montmorillonites SAz-1 (Cheto, Arizona, USA), SWy-2 (Wyoming, USA), Kunipia (Japan), Lastovce (Slovakia), one nontronite SWa-1 (Washington, USA), a hectorite (SHCa-1, California, USA), an illite/smectite (Dolná Ves, Slovakia), a kaolinite (Gold Field, Tanzania, Africa) and a pyrophyllite (Víglašská Huta, Slovakia) were studied. The dissolution was performed in 0.5M and in 6M HCl for 1 to 36 hours. The first group of the samples (Kunipia, SWy-2, Lastovce, Dolná Ves, Víglašská Huta and Gold Field) was treated with 6M HCl at 95°C, the second group with 6M HCl at 80°C (SAz-1, SWa-1) and the third group was dissolved in 0.5M HCl at 80°C (SHCa-1).

The solid reaction products were studied by infrared (IR) spectroscopy in the mid-IR (MIR, 4000–400 cm^{-1}) and the near-IR (NIR, 11000–4000 cm^{-1}) regions. This method provides unique evidence on the depopulation of the octahedral sheets and on the amount of SiO_2 , the reaction product of acid treatment.

The MIR spectra of original clay minerals contain a complex band near 1030 cm^{-1} due to characteristic stretching vibrations of Si–O groups. An upward shift of this band to the position of amorphous SiO_2 (near 1100 cm^{-1}) was observed as a result of acid treatment. Depopulation of the octahedral sheets was confirmed by decreasing intensities of the bands related to vibrations of the octahedral atoms, i.e., OH stretching vibrations near 3620 cm^{-1} , OH bending

vibrations absorbing in the 950–800 cm^{-1} region (AlAlOH near 915 cm^{-1} , AlFeOH near 880 cm^{-1} , AlMgOH near 845 cm^{-1} and FeFeOH near 820 cm^{-1}) and the band near 520 cm^{-1} , attributed to deformation vibration of Si–O–Al. Increasing intensity of the band near 800 cm^{-1} reflected growing amount of amorphous SiO_2 . The bands present in the NIR region result of overtones and combinations of fundamental stretching and deformation vibrations. Strong band at 7060 cm^{-1} was assigned to the 2ν-OH overtone of the OH-stretching vibrations. The decrease of OH overtone signalized loss of octahedral atoms from the structure. On the other hand, the appearance and rising intensity of Si–OH overtone near 7315 cm^{-1} provided evidence on protonization of Si–O groups. Acid treatment caused different level of structural decomposition of the clay minerals. The trioctahedral smectite (SHCa-1) was very unstable in the acid. Si–O stretching band was shifted to 1098 cm^{-1} after 8 h dissolution even in 0.5M HCl at 30°C. The dioctahedral smectites (SAz-1, Kunipia, SWy-2, Swa-1 and Lastovce) were more stable during acid dissolution. Their Si–O stretching bands were shifted to 1095 cm^{-1} (SAz-1), 1056 cm^{-1} (Kunipia), 1065 cm^{-1} (SWy-2), 1094 cm^{-1} (Swa-1) and 1100 cm^{-1} (Lastovce) after dissolution in 6M HCl at 80 and 95°C for 8 h. On the other hand, pyrophyllite, kaolinite and partially illite/smectite were more resistant to acid attack than smectites under the same conditions. Si–O stretching bands of pyrophyllite, kaolinite and illite/smectite after 8h HCl treatment were at the same positions as in the spectra of the original samples. No isomorphous substitutions of central atoms and thus no negative charge on the layers of pyrophyllite and kaolinite as well as partially collapsed interlayers of illite/smectite restricted the attraction of protons to penetrate into the layers and attack the OH groups.

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The equilibrium isotherm for lead removal by natural zeolite-clinoptilolite: a comparison of batch and column methods

Jelena PERIĆ, Nediljka VUKOJEVIĆ MEDVIDOVIĆ and Marina TRGO

Natural zeolite clinoptilolite has the property of ion exchange of its own hydrated Na, K, Ca and Mg ions with heavy metal ions from water solutions. The ion exchange process can be performed by the batch method or by the column method. This paper compares the equilibrium experimental results for ion exchange of lead ions on natural zeolite clinoptilolite, given from two different experimental performances by the batch and by the column method. Experiments were carried out at the same temperature ($t=20^{\circ}\text{C}$), with aqueous solutions of different initial concentrations of lead ions (for the batch method: $\gamma_0=103.5\text{--}2610.3\text{ mg/l}$; for the column method: $\gamma_0=212.5\text{--}520.5\text{ mg/l}$) (VUKOJEVIĆ MEDVIDOVIĆ et al., 2006). The removal efficiency for the batch method decreases with the increase of the initial concentration of lead ions, while remaining constant for the column method. The equilibrium points of both performances were tested with linear equations of Langmuir and Freundlich isotherms, in order to define the mechanism of binding of lead ions on the internal and external zeolitic particle surfaces. Figure 1 indicates the applicability of each isotherm type for a particular method.

The experimental points fit the Langmuir isotherm model better than the Freundlich one for batch and column

experimental performance. The better fit of the Langmuir isotherm equation indicates that removal of lead ions by natural zeolite clinoptilolite occurs on a homogeneous surface, by monolayer sorption on internal and external particle surfaces, with a finite number of identical sites, and with no interaction between bound ions. The Langmuir model is used for calculation and comparison of exchange capacities that equal 149.25 mg Pb/g for the batch method and are somewhat higher and equal 175.44 mg Pb/g zeolite for the column method, which is one of advantages of latter method for its practical application in wastewater treatment (AKSU & GONEN, 2004).

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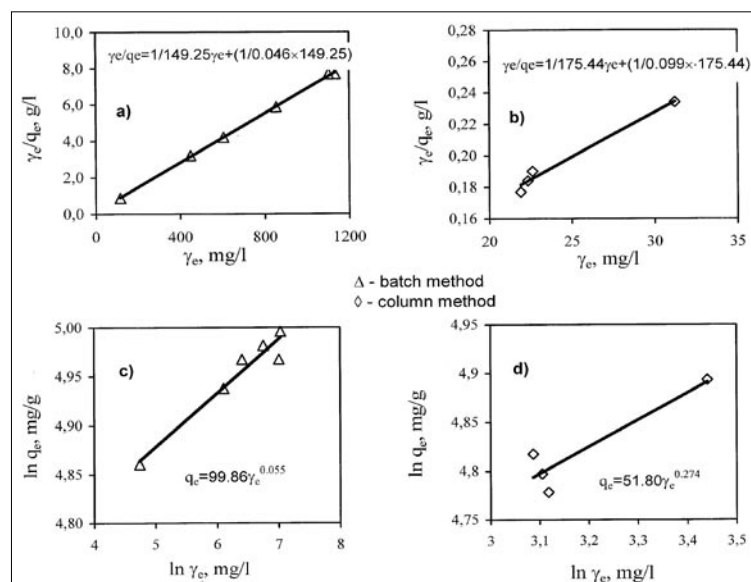


Fig. 1 Comparison of: a, b – Langmuir isotherm model; c, d – Freundlich isotherm model; a, c – batch method; b, d – column method.

Clay mineralogy and crystallochemistry of the Douro Carboniferous Basin (Early Stephanian C; NW Portugal)

Ary PINTO DE JESUS¹ and Fernando ROCHA²

The Douro Carboniferous Basin [DCB] (NW Portugal) is an intramontane basin from the Early Stephanian C and occurs in the geological setting of the Central Iberian Zone (CIZ). The DCB is the major Carboniferous basin present in the Douro–Beira Carboniferous Trough [DBCT]. With an extension of 53 km, the DCB extends in a narrow strip, always less than 500 m wide. The main tectonic structure is a duplex related with the tectonic deformation phase from late Hercynian orogeny (PINTO DE JESUS, 2001). In good relation with the granitoids occurring in the region, the coalification reached the meta-anthracite rank (LEMOS DE SOUSA, 1978; PINTO DE JESUS, 2001). In this work we present the results and conclusions about the research on the clay mineralogy of the several lithofacies of the DCB, and also from the studies on illite crystallinity (Kubler index [KI]). For those purposes, 24 samples (whole sample and <2 µm) were studied by X-ray diffraction, applying criteria and methods of MELLINGER (1979), and PEVEAR & MUMPTON (1989), and, for KI those of KUBLER (1964) and KISCH (1991).

Quartz and mica/illite are largely represented. Pyrophyllite is also present in several samples, sometimes in relevant amounts. Correlation between KI and the vertical succession was carried out with very good results. From these results, we were able to establish sedimentologic and stratigraphic subdivisions in the total series. It was also possible to confirm the position of the coalification as being in the transition from diagenesis to low-grade metamorphism domains (PINTO DE JESUS et al., 1997; ROCHA et al., 2000). KI values clearly show the rising of illite crystallinity in good relation with the increase of the coal rank. From these results, duplication on stratigraphic record was confirmed. Aiming a more refined sedimentological in-

terpretation, the obtained results were submitted to multivariate statistic analysis, namely principal components and discriminant analysis. The results obtained for the KI and the good correlation with those obtained by organic petrography, namely the vitrinite reflectance, related to the sedimentological and tectonic evolution of the DCB, lead us to conclude about the two main phases of coalification. The first one occurred before tectonic deformation and the late and more intense one related to a post-tectonic stage.

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Sorption equilibrium of phosphate anion on $Mg_xZn_{3-x}Al$ -type hydrotalcites

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Introduction

The presence of phosphate anion in surface water leads to serious problems of eutrophication, which require the decrease of phosphate concentration to stipulated limits.

The structure of the layered double hydroxides (LDHs) consists of positively charged brucite-like octahedral hydroxide layers, which are neutralized by the interlayer anion and water molecules. There is a large variety of cation pairs that can form hydrotalcite-type anionic clays; the only rule is to have the cationic radius similar to that of Mg^{2+} cations. As a result there is a wide variety of cation pairs, $M(I)M(III)$, $M(II)M(III)$, $M(II)M(IV)$, $M(III)M(IV)$, which can host a variety of anions. The interlayer anions and water molecules can be exchanged with other anions, so hydrotalcites are good anionic exchangers (LAZARIDIS, 2003; SEFTEL et al., 2005). Therefore, these compounds can be used for the advanced treatment of aqueous solutions with high content of anionic pollutants.

The aim of this work is to investigate the sorption equilibrium of phosphate anion on $Mg_xZn_{3-x}Al$ -type hydrotalcites.

Experimental

The sorption experiments were performed on activated $Mg_xZn_{3-x}Al$ hydrotalcite samples, where $x=3; 2; 1.5; 1; 0$. In order to study the retention capacity at equilibrium, identical amounts of synthesized solids were contacted with identical volumes of aqueous solutions containing phosphate anion. The solid/liquid ratio was 1 g/l. The samples were maintained at constant temperature ($25 \pm 1^\circ C$) in a

Shaker Bath thermostat for 12 hours in order to reach the sorption equilibrium.

Results and Discussion

The aim of the equilibrium experiments was to determine the sorption capacity of the mixed oxides for the adsorption of phosphate anion and to establish a selectivity order for all synthesized solids. Figures 1 and 2 show the sorption equilibrium of phosphate anion on two of synthesized samples.

The adsorption equilibrium models used were the general purpose Langmuir and/or Langmuir-Freundlich equations. The obtained values for the adsorption capacity of the type $Mg_xZn_{3-x}Al$ mixed oxides for the studied anion allowed to establish the selectivity order for synthesized samples. The selectivity order was: $Mg_3Al > Mg_2ZnAl > Mg_{1.5}Zn_{1.5}Al > MgZn_2Al > Zn_3Al$. Also, the maximum values of the adsorption capacity were determined. These ranged between 108 mg/g for Mg_3Al sample and 74 mg/g for Zn_3Al sample, respectively.

Acknowledgments: The authors wish to thank the MATNAN-TECH Scientific Authority (Project No.1/S1-2005) for supporting this research.

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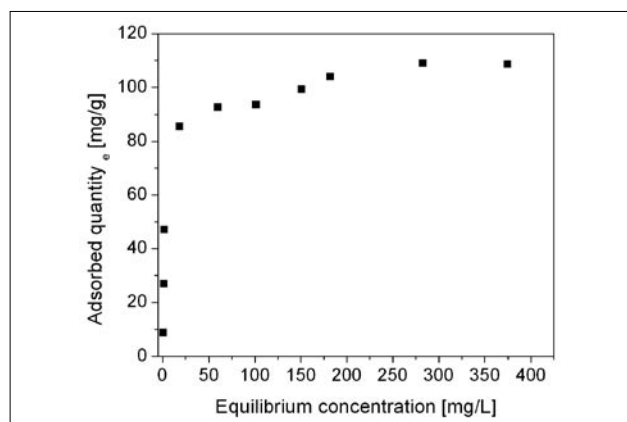


Fig. 1 Sorption isotherm of the phosphate anion on Mg_3Al sample.

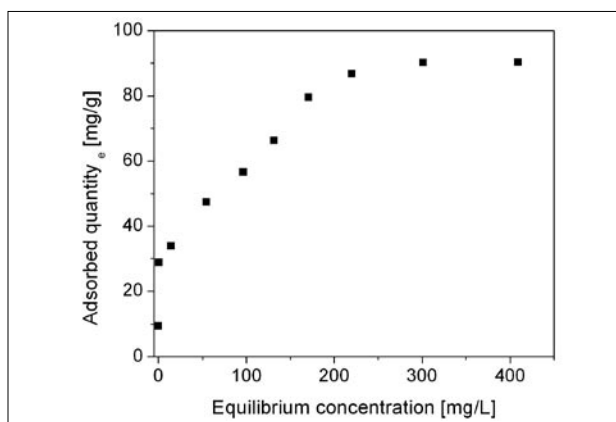


Fig. 2 Sorption isotherm of the phosphate anion on $Mg_{1.5}Zn_{1.5}Al$ sample.

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The TOT layer silicate of the lacustrine green clay, Rona limestone, Romania

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The IMA nomenclature of micas (RIEDER et al., 1998) offered a chemical framework for standardised species definitions, containing formal borders between glauconite and celadonite, as well as borders and gaps between the Al- and Fe-rich phases of the system. Recent investigation of uncommon occurrences of green TOT phases (e.g. HOVER & ASHLEY, 2003; TIBLJAŠ et al., 2004) challenge the IMA phase limits. More likely, these minerals occupy a continuous crystal chemical space (WEISZBURG et al., in prep.).

The green clay occurrence under study is hosted by the Rona Member of the Paleocene Jibou Formation (CODREA & SĂSĂRAN, 2002), a lacustrine lens-shaped body of local extension within the thick pile (over 1500 m) of continental red silty clays. The classical profile of it is located in the Rona village, near Jibou town (Sălaj district, Romania). The succession consists of a lacustrine and a palustrine association; dolomitisation processes identified in several carbonate sequences point to an advanced degree of diagenesis.

The Rona Member contains, at several levels, local centimetre-size accumulations of green clays, mainly related to cracks and fractures in the host rock. In the basal part of the Rona profile, in a 40 cm thick limestone level – consisting of dominant calcite and subordinate dolomite, as proven by the bulk XRD pattern – beside void-filling, the green clay forms coatings, in average 0.5–1 cm thick, around nodular cherts. The silica nodules, 4–20 cm in size, are polychromatic and inside exhibit “septaria”-like networks of whitish radial and polygonal cracks. The studied samples originate from these coatings.

Powder XRD revealed that the green clay represents a mixture of dominant Fe-rich 10 Å phyllosilicate, calcite (~30%) and quartz (~5%). The Fe-rich mica was separated from the green clay by careful decarbonation procedure (applying 5% acetic acid), and then investigated by XRD, IR and Mössbauer spectroscopy, TEM and ICP–AES. In the XRD pattern, the symmetric 001 reflection and the d_{060} value (1.509 Å) point to the celadonitic nature of the studied material. The IR spectrum is characterised by two

strong adsorption bands (3557 and 3525–33 cm⁻¹) in the OH-stretching region, corresponding to ν Fe³⁺–Mg–OH and ν Fe³⁺–Fe²⁺–OH vibrations in celadonite–XC (for the suffices see WEISZBURG et al., in prep.). The Mössbauer spectrum is rather simple, it can be fitted for two doublets, assigned to octahedral environments of Fe³⁺ and Fe²⁺, respectively. The crystal chemical formula –

$K_{0.71}Na_{0.02}Ca_{0.05}(Fe^{3+}_{0.89}Mg_{0.62}Al_{0.27}Fe^{2+}_{0.25}Ti_{0.01})(Si_{3.89}Al_{0.11}O_{10}(OH)_2)$ (assuming the presence of 3 wt% quartz) – defines a glauconite–GC mineral, close to the border with celadonite–CC.

Few studies are currently available on the mineralogy and genesis of lacustrine green clays. According to the IMA criteria, the TOT component of such clays plots in the non-defined field between illite and glauconite (PORRENGA, 1968; HOVER & ASHLEY, 2003), in the aluminoceladonite and celadonite fields (HOVER & ASHLEY, 2003) or in that of glauconite (present study). It seems that the lacustrine environments provide a wide range of physical, chemical and possibly biologically-mediated mechanisms that may direct neof ormation of green TOT clays of a wide range of chemistries.

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Sorption kinetics and equilibrium of thiocyanate anion on $Mg_xZn_{3-x}Al$ -type hydrotalcites

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Vasile PODE² and Elena Mihaela SEFTEL¹

Introduction

Thiocyanate containing wastewaters result in a variety of industrial processes such as: herbicide and insecticide production, acrylic fibre production, manufacturing of thiourea, electroplating, etc. The removal of thiocyanates from wastewater is a must since this anion is well-known as a priority dangerous pollutant.

The anionic clays type hydrotalcite compounds have gained a large importance in pollution abatement techniques, due to sorption and catalytic properties (GUPTA, 1998). The interlayer anions can be exchanged with other anions, so hydrotalcites are good anionic exchangers. Therefore, these compounds can be used for the advanced treatment of aqueous wastes with high content of anionic pollutants

This paper aimed the thermodynamic and kinetic characterization of the sorption process of thiocyanate anion on $Mg_xZn_{3-x}Al$ -type hydrotalcites.

Experimental

The hydrotalcite samples were prepared by co-precipitation of Mg(II) and/or Zn(II) and Al(III) nitrate solutions, at constant pH and room temperature followed by heating at 80°C for 18 hours. The sorption experiments were performed on the activated samples at 450°C for 2 hours using $Mg_xZn_{3-x}Al$ -type hydrotalcites, where $x = 3; 2; 1.5; 1; 0$. The sorption equilibrium was studied at $25 \pm 1^\circ C$ using a Shaker Bath thermostat for 12 hours. The kinetics study was performed for an aqueous with concentration of 75 mg SCN-/l.

Results and Discussion

The aim of the equilibrium experiments was to determine the sorption capacity of the hydrotalcite samples for the

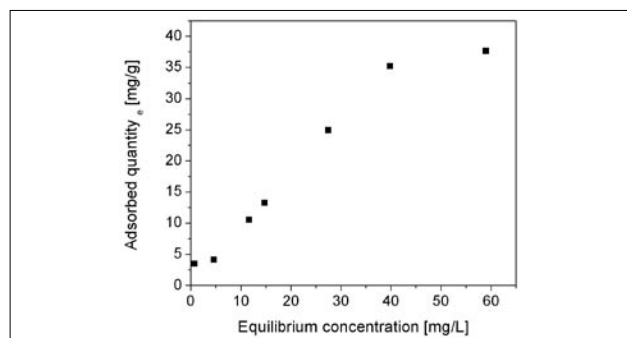


Fig. 1 Sorption isotherm of the thiocyanates anion on Mg_3Al sample.

adsorption of thiocyanate anions. Various theoretic models were suitable for the experimental equilibrium data. The sorption capacity ranged from 12.7 mg/g for Zn_3Al to 37 mg/g for Mg_3Al . The values of sorption capacities allowed to determine the selectivity serie of synthetised materials for studied anion, i.e., $Mg_3Al > Mg_2ZnAl > Mg_{1.5}Zn_{1.5}Al > MgZn_2Al > Zn_3Al$. Figure 1 shows the sorption isotherm for Mg_3Al sample.

The results of the kinetic experimental data were reached based on Lagergren equation (LAZARIDIS, 2003), expressed as:

$$q_t = q_e [1 - \exp(-kt)] \quad (1)$$

where: q_t – sorption capacity at the time t , $mg\ g^{-1}$; k – kinetic rate constant, h^{-1} .

The kinetic curve corresponding the sorption process of thiocyanate on Mg_3Al is shown in Fig. 2. The anion kinetic sorption results were fitted satisfactory with the Lagergren equation.

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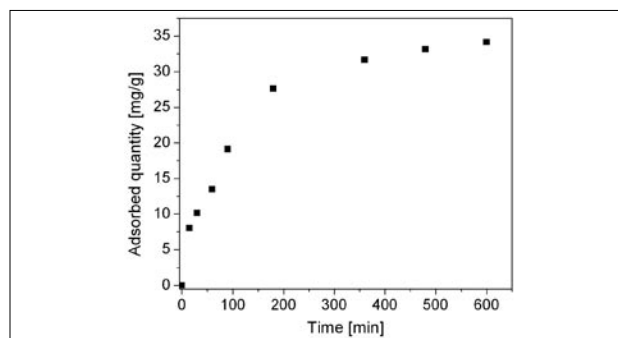


Fig. 2 Kinetic curve of thiocyanates anion sorption on Mg_3Al sample.

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Use of Romanian clays for textile wastewater depollution

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Introduction

Synthetic azo-dyes are extensively used for dyeing and printing in textile industries (YANG, 2005). The traditional textile finishing industry consumes about 100 l of water to process about 1 kg of textile materials. Wastewater from textile industries creates great problem of pollution due to the dyes contained therein. The dyes contribute to the organic load and toxicity of the textile industry effluents. In the same time, the dyes are normally present in dyehouse effluent at concentrations of 10–50 mg/l, color being notable at concentrations above 1mg/l.

Generally, chemical, physical, biological, catalytical and photocatalytical methods have been used for removal or dye destruction from dye containing wastewater (ZHOU & SMITH, 2002).

In this study, the adsorption and photodegradation of Congo Red dye using natural and modified Romanian clay has been examined for the purpose of identifying the ability of these materials in removal of colored textile dyes from wastewater (YERMIYAHU et al., 2003).

Experimental

In this study raw Romanian clay (63% smectite) coming from Valea Chioarului area was used. In view of titanium intercalation, sodium-clay form having the following composition (% wt): SiO₂ – 72.87; Al₂O₃ – 14.5; MgO – 2.15; Fe₂O₃ – 1.13; Na₂O – 0.60; K₂O – 0.60; CaO – 0.90; PC – 5.70 and cation exchange capacity determined by ammonium acetate method, of 82 meq/100 g, as matrix, was used. For the preparation of the TiO₂ – pillared clay, the alkoxide molecules were adsorbed onto/into clay samples

(1–14 mmol Ti/g clay) in a hydrochloric acid medium (MOGYORÓSI et al., 2003). The structure and properties of the obtained materials were studied by X-ray diffraction, FTIR spectroscopy and thermal analysis.

Results and Discussion

The adsorption of dye on the sodium montmorillonite shows a strong dependence on the pH and follows a Langmuir adsorption model. Photodegradation process was dependent on the effect of the initial concentration of dye, titania content and pH reaction medium. The reaction rate was ascertained and optimum conditions for maximum degradation were determined. The disappearance of the studied dye follows approximately a pseudo-first kinetic order according to the Langmuir–Hinshelwood model.

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Structure analysis of hydrotalcite intercalated with pyrenetetrakisulphonate acid, molecular simulations and experiment

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Present work is focused on complex structure analysis of hydrotalcite intercalated with pyrenetetrakisulphonate acid. Structure analysis of intercalates include theoretical methods (molecular simulations) and experimental methods (X-ray diffraction and thermo gravimetric measurements). Knowledge of structure is crucial for determination of properties and understanding of structure-properties relationship in design of new materials with desirable properties.

Intercalation in this case is based on ion exchange interaction. Interlayer anions, usually carbonate anions, are replaced by desirable organic anions to compensate the positive layer charge of hydrotalcite. Hydrotalcite has a suitable layer structure due to weak interlayer interactions and strong bonds among atoms in the layer. Big advantage of hydrotalcite layers is also simple preparation, possible layer modifications and low cost of preparation.

Structure of hydrotalcite intercalated with pyrenetetrakisulphonate acid was solved using modified SUPRAMOL program (KOUDELKA & ČAPKOVÁ, 2002) and Cerius² and Material Studio (CERIUS², 2000). Calculations are based on the energy minimization and geometry optimi-

zation. Structure is described by empirical force field parameters and suitable minimization strategies for this type of intercalate were created.

Combining modelling and experimental results we obtained a series of initial models from SUPRAMOL. These initial models were minimized and optimized for different basal spacing based on experimental data. Structure models were solved for three different samples: Sample 1 with basal spacing: 9.8 Å, sample 2 with basal spacing: 13.6 Å and sample 3 with two significant basal spacing: 11.7 Å and 12.8 Å. The results of modelling show that sample 3 was probably unstable. Individual models were calculated with amount of water molecules determined from thermo gravimetric measurements. The influence of interlayer water on the resultant crystal structure was investigated.

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Modification of the montmorillonite surface with cationic surfactants

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Phyllosilicates can be modified with quaternary salts including cationic surfactants in order to obtain new materials with exceptional properties for the retention of various organic contaminants (WEISS & KLIKA, 1994), oils and amines (BEALL, 2003), and even inorganic oxyanions (LI & BOWMAN, 2001). In this study a Na⁺-rich montmorillonite (MMT) type Wyoming ($\text{Al}_{3.4}\text{Mg}_{0.6}$) ($\text{Si}_{7.8}\text{Al}_{0.2}\text{O}_{20}(\text{OH})_4$) was used for the MMT modification with cationic surfactants, such as cetyltrimethylammonium bromide (CTMB) and cetylpyridinium chloride (CPC). Both surfactants were dissolved in water-ethanol (50:50, v/v) solutions in which MMT was added. Such prepared suspensions were shaken for two hours to reach adsorption equilibrium. The centrifuged and dried MMTs saturated with CTMB (CTMB-MMT) and CPC (CPC-MMT) were examined by the surface area and pore area measurements, electron scanning microscopy (SEM) and moisture adsorption.

Using the BET method, total surface areas of MMT, CTMB-MMT, and CPC-MMT were determined (Table 1). The 5–50 μm and 50–1000 μm pore size areas were estimated by means of a Dollimore Heal isotherm (DOLLIMORE & HEAL, 1964). The 0–5 μm pore area was calculated as a difference between the total and the 5–1000 μm pore area. The MMT pores of 0–50 μm were significantly reduced by the surfactant adsorption. On the contrary, a number of the 50–1000 μm pores in the modified montmorillonite samples increased.

Morphology of the natural and modified montmorillonite was examined by SEM. The SEM micrographs showed that the surface of MMT was equalized, covered by small and well separated particles. The CTMB-MMT and CPC-MMT surfaces exhibit a grain-like structure of agglomerated particles. The modified particles gather together more easily than the unmodified ones because the surfactants adsorbed compensate the MMT negative

surface charge and thus eliminate the repulsive electrostatic forces. In this way the large macropores were originated as demonstrated in Table 1.

The MMT surface modification was verified by a study of moisture adsorption and desorption isotherm plots obtained using a dynamic vapour sorption (DVS) method. Moisture sorption was expressed as the percentage moisture content as a function of relative humidity. In comparison with natural MMT, both CTMB-MMT and CPC-MMT exhibited very similar but significantly smaller amount of water taken up. The plots hysteresis loops of CTMB-MMT and CPC-MMT were narrower than that of MMT. It is surprising that only a slightly lower content of water was sorbed on CPC-MMT in spite of its about twofold increase of surface area (Tab. 1). This effect can be explained by the higher amount of CPC attached to the MMT surface forming the more hydrophobic surfactant coverage. It was also confirmed by construction of the CTMB and CPC adsorption isotherms from which it followed that MMT was saturated with the higher amount of CPC.

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Table 1 Natural and modified montmorillonite pore size distribution.

	MMT	CTMB-MMT	CPC-MMT
Total area (m ² /g)	28.50	4.40	8.83
0–5 μm pore area (m ² /g)	21.79	0.37	2.61
5–50 μm pore area (m ² /g)	6.37	2.81	4.40
50–1000 μm pore area (m ² /g)	0.34	1.22	1.82

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Climato-environmental controls on clay mineralogy of the Hettangian–Bajocian successions of the Mecsek Mountains (Tisza Mega-unit, Hungary)

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Clay mineralogy of ancient sedimentary successions is widely considered to be a powerful tool for interpreting weathering conditions and palaeoclimate in the source area. The Mecsek Mountains make part of the lowermost known nappe of the Tisza Mega-unit (Hungary) and have a well-developed succession of Jurassic sediments.

In the Early Jurassic (Hettangian–Sinemurian), fluvial and shallow marine coal-bearing siliciclastic rocks (Gresten facies, Mecsek Coal and Vasas Marl Formations) were deposited. The clay assemblages comprise predominantly kaolinite (kao), illite (ill) and illite/smectite (I/S) mixed-layer minerals with the presence of berthierine and/or chlorite. The relative proportions of kaolinite and berthierine in the Mecsek Coal Formation suggest a subtropical humid climate and a high supply of terrigenous clastics to the basin. The upper Sinemurian–Bajocian successions of the Mecsek Mountains are composed of predominantly hemipelagic mudstones (Allgäu facies, Hosszúhetény Calcareous Marl to Komló Calcareous Marl Formations) with variable proportions of carbonate and organic matter. These deposits show occasional intercalations of redeposited sediments and limestone bodies (Mecseknádasd Sandstone, Kecskéhát and Pusztakisfalu Limestone Formations), in

accordance with effects of eustatic sea level changes and intensive subsidence of depositional basin. The clay mineral suites of the Pliensbachian Hosszúhetény, Mecseknádasd and Kecskéhát Formations are composed predominantly of illite with subdominant amounts of kaolinite (kao/ill<1). I/S mixed-layer minerals are present in small proportion. Based on these results, the Pliensbachian time interval is interpreted to represent warm and seasonally humid (monsoon-like) climatic conditions and a moderate input of terrigenous clastics relative to the underlying formations. Towards the Toarcian, kaolinite becomes the dominant clay mineral (Óbánya Siltstone Formation; kao/ill>1) suggesting a humid climate and intense continental weathering related to the oceanic anoxic event. In contrast, the Bajocian Komló sediments contain high proportions of I/S mixed-layer minerals and illite with sparse occurrence of kaolinite and chlorite (kao/ill=0 or kao/ill<1). This clay mineral assemblage reflects warm and humid climatic conditions with seasonal droughts and a minor input of terrigenous clastics from a relatively distant source area.

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Mineralogy of Latosols along a regional toposequence across the Central Plateau (Brazil): First results

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Edi M. GUIMARÃES³ and Michel BROSSARD⁴

The Brazilian Central Plateau is constituted of the two main geomorphic surfaces: the South American surface and the Velhas surface. These surfaces were developed during the Cretaceous Superior and Tertiary and are covered by deeply weathered Latosols. The South American surface is the oldest and occupies the highest position in the landscape (950 to 1,200 m altitude) with smoothly convex plane portions. The Velhas surface is composed by irregular and slightly sloping planes and occupies in the landscape (750 to 950 m altitude). It is connected to the South American surface by areas of steep hillsides.

Latosols cover about 40% of the Central Plateau surface area. Most Latosols in the Brazilian Soil Taxonomy correspond to Oxisols in the Soil Taxonomy and to Ferralsols in the International Reference Base System. In the Central Plateau, the Latosols can be Red Latosols (Acrustox, ~28%), Yellow Red Latosols (Acrustox, ~10%) and Yellow Latosols (Haplaquox, ~2%). The main characteristics of Latosols are a poor differentiation of the horizons, a weak macrostructure and a strong submillimetric granular structure resulting in microaggregates 50 to 300 µm in size (REATTO et al., 2000). The objective of this work was to discuss the first results of the mineralogical characterization of Brazilian Latosols located along a regional toposequence across the Central Plateau.

Ten Latosols (L) developed in different parent materials were selected along an approximately 350 km long regional toposequence across the South American Surface (L1 to L4) and Velhas Surface (L5 to L10). Samples were collected in the diagnostic horizon (Bw) of these Latosols. Basic soil characteristics were determined on the air-dried <2 mm material according to the Brazilian standard procedures (EMBRAPA, 1997). Thus, the particle size distribution was determined using the pipette method after dispersion with NaOH 1N. Chemical composition obtained after dissolution in sulfuric acid was used to estimate the kaolinite, gibbsite, goethite and hematite content. Goethite and hematite content was also estimated using the soil color (hue, value and chrome). The mineralogical composition of the

<2 µm fraction was also determined by using X-ray diffraction and results confirmed those recorded after chemical dissolution. The relations Ki and Kr that are weathering indices (EMBRAPA, 1997) were computed as following:

$$K_i = 1.7 (\text{SiO}_2/\text{Al}_2\text{O}_3)$$

and

$$K_r = 1.7 (\text{SiO}_2)/(\text{Al}_2\text{O}_3 + 0.6375 \times \text{Fe}_2\text{O}_3)$$

The Latosols studied showed Ki and Kr that ranged from 0.32 to 1.36 and from 0.26 to 1.06 respectively. The averaged Ki and Kr were 0.50 and 0.40 respectively on the South American Surface with Latosols whose parent materials were originated from lateritic crusts and saprolites of detritic and mafic granulite rocks. The averaged Ki and Kr were 1.10 and 0.86 respectively on the Velhas Surface with Latosols whose parent materials originated from colluvial pediments from South American Surface and saprolites of pelitic rocks. The ratio kaolinite/kaolinite+gibbsite (RKGb) ranged from 0.24 to 0.78, and the averaged RKGb was 0.35 on the South American Surface and 0.70 on the Velhas Surface. The ratio hematite/hematite+goethite (RHGt) ranged from 0 to 1, and the averaged RHGt was 0.36 on the South American Surface and 0.74 on the Velhas Surface. The kaolinite content ranged from 20 to 65 g.kg⁻¹ for the Latosols studied, the averaged content being 28 g.kg⁻¹ for Latosols located on the South American Surface and 55 g.kg⁻¹ for Latosols located on the Velhas Surface. The gibbsite content ranged from 22 to 63 g.kg⁻¹, the averaged content being 52 g.kg⁻¹ for Latosols located on the South American Surface and 27 g.kg⁻¹ for Latosols located on the Velhas Surface.

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Relationship between heavy metals and clay in Spanish agricultural topsoils

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Soil clay plays an important role in the explanation of heavy metal contents in soils. In this work 624 samples were collected from an 8 km² terrain in the Ebro basin (Spain). The granulometric composition, the content of seven heavy metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn) and other parameters (pH, organic matter and carbonates) were quantified in agricultural topsoil. Significant correlation exists between heavy metals and soil parameters (BOLUDA, 1988; ALLOWAY, 1995). This study shows the spatial correlations and variations in these heavy metals measured in connection with the percentage of clay fraction in soils.

The natural concentration of heavy metals in arable soil depends primarily on the geological parent material composition (DE TEMMERMAN et al., 2003). However, clay content generally influences the concentration of these elements. The average concentrations (mg/kg) obtained were: Cd 0.415±0.163, Cr 20.27±13.21, Cu 17.33±14.97, Ni 20.50±22.71, Pb 17.54±10.41, Zn 17.53±24.19 and Hg 35.6±42.05 µg/kg. The distribution manner of individual associations of elements in topsoils was determined by principal components method. The first factor, explaining 38.46% of the total variance, was strongly and positively related to Pb, Cu, Zn, Hg and Cd. The second factor, explaining 18.50% of the total variance, showed high positive factor loadings on Cr and Ni. Both factors show a significant correlation with clay content ($r^2=0.24$ and $r^2=0.39$ respectively).

The clay (<2 µm) and silt (2–63 µm) fractions were determined by the pipette method (sedimentation). Correlation analysis was carried out to determine the extent of the relationship between the elements investigated and clay percentage in soils. There is a strong correlation between clay and heavy metals content. Many of the correlation coefficients are significant (Clay/Pb, Clay/Cu, Clay/Zn, Clay/Cd) and some are very strong (Clay/Cr with $r^2=0.42$ or Clay/Ni with $r^2=0.35$). These results were similar to those obtained by BOLUDA (1988) who demonstrated significant correlations among some heavy metals and clay content, between

these metals and organic matter and a negative correlation with carbonates. Metal deficiency is associated with sandy, shallow soils over chalk and peaty soils (NICHOLSON et al., 2003). The textural classes ranged from sand through loam to clay and these granulometric fractions were related to heavy metal concentrations as expected. The heavy metals concentrations were higher for clay soil than sand or loam soil. DE TEMMERMAN et al. (2003) obtained the same result for background values of Cr, Ni, Zn and Cu, although not for Cd.

Another high relationship was found between organic matter and heavy metals content. The soil is predominately agricultural and has a low organic matter content (average 1.9%; range between 0.2% and 13.1%). Higher percentage of organic matter was observed only in the grassland topsoils. Organic matter has also been found to influence heavy metal absorption in soils; this effect is probably due to the cation exchange capacity of organic material (TICHY et al., 1997; MARTIN & KAPLAN, 1998).

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Phase transformations of Co–M^{III} layered double hydroxides (M^{III} = Al, Cr, Fe, or Mn) during thermal treatment

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Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds or anionic clays, are decomposed to form well-dispersed homogeneously mixed oxides suitable for application in heterogeneous catalysis. Therefore it is of interest to understand in detail the thermal behaviour of these materials. Four LDH precursors containing Co in combination with various trivalent cations (Al, Cr, Fe, or Mn) were prepared by coprecipitation of corresponding nitrate solutions, where the Co/M^{III} molar ratio of 2 was adjusted. Thermal decomposition of prepared LDHs and phase transformations of related mixed oxides were studied using thermal analysis (TG/DTA/EGA), powder X-ray diffraction including high-temperature measurements (HT XRD) and Raman spectroscopy. A well-crystallized hydrotalcite-like phase was detected in Co–Al and Co–Fe samples, the Co–Cr sample exhibited a lower crystallinity. The lattice parameters evaluated from diffraction data increased with increasing M^{III} cationic radius, which indicated an incorporation of M^{III} cations into the hydroxide layers of hydrotalcite-type lattice. In the XRD pattern of Co–Mn sample, an unidentified phase with $d \sim 0.665$ nm was found. Two major endothermic effects, characteristic for hydrotalcite-like compounds, were found in DTA curves. The first one was ascribed to release of interlayer water. The second endothermic effect, accompanied by simultaneous H₂O and CO₂ evolution, was ascribed to dehydroxylation of hydroxide layers and destruction of LDH structure. The dehydration and dehydroxylation processes partially overlapped, especially in the case of Co–Fe sample. Thermal stability of prepared LDHs increased as follows (temperatures of endothermic minima corresponding to LDH thermal decomposition are written in parenthesis): Co–Fe (190°C) < Co–Al (260°C) \approx Co–Cr (265°C). During heating of Co–Mn sample, also two major endothermic effects with minima at approximately 100 and 245°C were observed and the course of DTA curve was similar to that measured with LDH samples. However, both these minima were associated with evolution of water, which can be explained by dehydroxylation of unidentified, probably hydroxide- and/or oxohydroxide-type phases.

According to XRD results, the prepared LDHs were decomposed at temperatures up to 200°C. The HT XRD measurements showed a slight decrease of LDH basal spacing due to a partial dehydration, but the dehydration temperatures indicated by HT XRD were of about 30–40°C lower than those detected by thermal analysis (the same

heating rate was used). Thermal decomposition accompanied by collapse of LDH structure resulted in a formation of nanocrystalline spinels. Spinel was formed also after thermal decomposition of the Co–Mn sample. Based on the XRD data processing the lattice parameters and mean coherence length were evaluated. With increasing calcination temperature, a gradual crystallization of spinel-like mixed oxides was observed but the composition of spinel phases was partially changed. The ratio of integral intensity of (111) and (220) diffraction lines can be taken for evaluation of the occupancy of tetrahedral cationic sites by a lighter component (WOLSKA et al., 1997). XRD data processing showed that the occupancy of tetrahedral cationic sites by light component (e.g. Al) increased with increasing calcination temperature. Raman spectroscopy confirmed the presence of Al cations in the tetrahedral sites of spinels obtained already at low calcination temperatures (the characteristic band at 727 cm⁻¹ was detected in the Raman spectra of these samples).

The Co-rich spinels, i.e. Co₃O₄ or slightly M^{III}-doped (Co_{1-x}M^{III}_x)₃O₄ exhibit four characteristic sharp bands at 300–800 cm⁻¹ and therefore they can be easily identified by Raman spectroscopy. A segregation of Co-rich spinels was observed in samples obtained at lower calcination temperatures (300–600°C). In some cases, this phase segregation cannot be detected by XRD because the lattice parameters of formed spinels are very close to each other. With increasing calcination temperature, a recrystallization of the primary formed Co-enriched spinels took place and an incorporation of M^{III} cations into the spinel lattice can be considered. The mixed oxides with spinel structure were detected in powder XRD patterns of samples calcined up to ca. 900°C. At high temperatures above 900°C, the phase transformation was observed, when CoO was formed to the detriment of spinels.

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Altered tephra layers in the Upper Jurassic Lemeš deposits near Maovice (Dalmatia, Croatia): clay mineralogy and basic soil mechanic properties

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Upper Jurassic Lemeš deposits in the External Dinarides are the sedimentary succession comprised of light coloured platy limestones (VELIĆ et al., 1995) and/or dolomitic limestones and dolomite (BRAUN, 1991) with chert intercalations. The succession clearly deciphers different facies development than those regularly being formed within the Adriatic–Dinaric carbonate platform realm throughout the Mesozoic. It is assumed to have been moulded along the intraplatform troughs connected to the open sea.

Two bentonite layers in the vicinity of Maovice village in the Dalmatian hinterland intercalate within typical Lemeš deposits (BRAUN, 1991). The material for investigations has been sampled from the more despicably situated bentonite layers on the localities Bunarić and Gornji Ždanj. The preliminary results of our research on bentonite layers mineralogy and bentonite soil mechanic properties are briefly reported herein.

The XRD analysis of global samples reveals montmorillonite as the principal mineral in both samples accompanied by calcite, cristobalite, plagioclase (albite?), quartz and biotite in the Bunarić sample and calcite, quartz, clinoptilolite and cristobalite in Gornji Ždanj sample. Total carbonate contents were determined to 8.06 wt.% and 26.49 wt%, respectively. Montmorillonite is defined by treatment in oriented samples from diffraction maximums showing $d_{(001)}=14.84 \text{ \AA}$, $d_{(001)}=15.02 \text{ \AA}$ (air dried), $d_{(001)}=16.69 \text{ \AA}$, $d_{(001)}=16.62 \text{ \AA}$ (ethylene glycol saturated), $d_{(001)}=9.79 \text{ \AA}$, $d_{(001)}=9.59 \text{ \AA}$ (heated) for Bunarić and Gornji Ždanj samples, respectively. Alteration of tephra to the assemblage of exclusively montmorillonite and zeolite from the heulandite family ($\text{Ca}_{0.54}\text{Na}_{0.08}\text{K}_{0.09}\text{Ba}_{0.03}[\text{Al}_{1.63}\text{Si}_{7.46}\text{O}_{18}]\cdot 6\text{H}_2\text{O}$ after microprobe measurement) suggests diagenesis at around pH~8, typical for the relatively deep marine setting within the carbonate platform.

In the grain size fraction 63–125 μm , the sample from Bunarić contains comparatively high amount of volcanic crystalloclasts. The most abundant are euheudral biotite ($\text{Mg}\#=55.8\text{--}61.3$; $\text{TiO}_2=4.2\text{--}4.7 \text{ wt.}\%$, $\text{BaO}=0.18\text{--}0.58 \text{ wt.}\%$) and sanidine ($\text{Or}_{65.9\text{--}74.9}\text{Ab}_{24.4\text{--}33.5}\text{An}_{0.65\text{--}1.34}$)

whilst quartz, subcalcic augite ($\text{Wo}_{36.5}\text{En}_{41.1\text{--}41.5}\text{Fs}_{22.0\text{--}22.3}$), hyperstene ($\text{Wo}_{1.6}\text{En}_{59.2}\text{Fs}_{39.2}$) and potassium tschermakite are occasionally observed. Radiolarian fossils are abundant in both samples. Volcanoclastic mineral composition and mineral chemistry of the Lemeš deposit tephra layers strongly suggest a high-K calc-alkaline (rhyolitic?) volcanic arc as the source of tephra. Apparently similar composition of the volcanic crystalloclasts might be an indicator of tephra input related to the eruption(s) from a single regional source.

According to the grain size composition and content of calcite Bunarić sample is classified as clayey silt (clay 30%, silt 66%, sand 1%, gravel 3%) and Gornji Ždanj sample as calcareous silty clay (clay 52%, silt 40%, sand 6%, gravel 2%) in classification scheme after KONTA (1969).

Soil mechanic properties are being reported for Bunarić and Gornji Ždanj respectively. Measured dry densities are set to 2.59 Mg/m^3 and 2.64 Mg/m^3 , while weight densities are 25.43 kN/m^3 and 25.91 kN/m^3 . Plastic limits of tested material are 45.54% and 36.65%, with liquid limits set to 86.85% and 104.82%. Increases of soil volume after the free swell test are up to 87% and 92%. The oedometer consolidation test showed modulus of compression for stress increment from 100 kPa to 200 kPa nearly 3.8 MPa and nearly 2.5 MPa. Overall soil mechanic tests data clearly imply high compressibility, high swell aptitude and wide range of plastic state of analyzed bentonites.

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Properties of clay mineral surfaces modified by intensive physical disintegration

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Previous studies have shown that surface and bulk properties of minerals can be modified by physical wear causing particle size diminution (SONDI & PRAVDIĆ, 1997, 2002). These processes, often called “physical weathering”, continuously occur in nature and result in alteration of size, morphology, and bulk properties of mineral components. The present study reviews research on the effect of physical disintegration on the alteration of the structural and surface properties of three different types of clay minerals – kaolinite, Otay-montmorillonite and chlorite-ripidolite.

The structural properties of milled samples were examined by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). Their surface properties were determined by measuring the electrophoretic mobility (EP, $\text{m}^2\text{s}^{-1}\text{V}^{-1}$), specific surface area (SSA, m^2g^{-1}), and cation exchange capacity (CEC, $\text{meq}/100\text{g}$).

This study has shown cases where physical disintegration leads to size diminution, alloying processes, and for-

mation of an amorphous phase followed by changes in the morphology, structure and surface properties of clays.

The milling approach simulates processes that take place in nature – the processes of intensive physical disintegration which produce nanosize clay particles of undetermined structure and of unique surface properties. Such particles are the most reactive mineral phase in natural environments and this characteristic governs physico-chemical interactions at mineral surface/aqueous medium interfaces in soils and aquatic sediments.

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Total surface area, surface charge density, cation exchange capacity and water retention in smectites

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A study of 12 smectite clays (<0.2 μm fractions) with a range of layer charge was undertaken to investigate the amount of water held at different temperatures, and to use these data for refining the relationship between the total surface area, cation exchange capacity, and charge density (TSA/CEC/Q). The samples were treated to remove iron oxide and carbonate impurities, Ca-exchanged, dialysed, analyzed by ICP, and their structural formulae were calculated. From the structural formulae and *b* parameter of the unit cell, measured by XRD, densities and total surface areas of the clays were obtained. Water retention by Ca-smectites was studied by TGA–MS experiments carried out from room temperature to 900°C, after the samples were equilibrated at 47% RH. Standard CEC measurements were made by the Co-hexamine method and EGME sorption measurements were also performed. TSA and Q obtained from chemical formulae were used to calibrate techniques of TSA measurement based on water and EGME sorption.

TGA–MS data show that molecular water is held by some smectites even above the onset of dehydroxylation. The amount of water lost up to 200°C approaches closely the monomolecular coverage of the clay surface. Water lost above 200°C is close to 11% of this mass, and water lost up to 110°C (conventional temperature of CEC and TSA measurements) amounts to 81–92% of this mass. Q val-

ues calculated from CEC and TSA were substantially lower than Q obtained from the formulae. These differences were almost eliminated when the water data were used to recalculate CEC to the completely dry clay basis.

TSA from the structural formulae were used to calculate H₂O and EGME retentions on clay surfaces (in mg/m²). From the average values obtained, TSA_{H₂O} and TSA_{EGME} were calculated. The calculations were further refined using the experimental relations between H₂O and EGME retention and Q. CEC and H₂O retention, being both dependent on TSA and Q, were also used to calculate these two parameters by two equations with two unknowns. The errors of the different calculations are not correlated, so they are decreased if the results are averaged. For the refined calculations the average error of TSA_{H₂O} and TSA_{EGME} combined did not exceed 3%, and for the unrefined calculations (applicable when the structural formulae are not known) it increased to 4.5%.

TGA measurement of water held on clays up to 200°C, which is a necessary step in measuring total rock porosity from water content, thus provides an opportunity to measure TSA of the sample with precision comparable or better than the conventional EGME measurement.

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Identification of glauconite–smectite interstratification using computer simulations in NEWMOD® program

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Most X-ray diffraction (XRD) studies of glauconitic material (green pellets called glauconite) are based on XRD of random powder mounts. Despite the structure of glauconite (GL) seems to be close to that of illite–smectite mixed layer minerals (I–S), the papers concerning diffraction patterns obtained for oriented mounts are relatively rare (e. g. THOMPSON & HOWER, 1975; WIEWIÓRA & ŁĄCKA, 1980). It is widely accepted that XRD patterns of oriented mounts prepared for mixed layered clay minerals are most useful in characterization of the nature of component layers, and the ordering in *c* direction. The information obtained using this procedure is potentially useful in interpretation of the minerals origin, and their growth mechanism. The main idea behind this paper is to examine whether or not a computer simulation method using the NEWMOD® program (REYNOLDS, 1985), commonly used in case of I–S, is an effective way to reveal the structural details of glauconitic material.

Samples were collected from sandstones of the Matura Beds of the Polish Flysch Carpathians. After disaggregation of rocks, a magnetic separation was used to produce concentrates containing only glauconitic grains. The material was then purified using acetate buffer and ultrasonic treatment. Cleaned glauconites were separated by heavy-liquid fractionation into three density fractions: 2.8–2.7 g/cm³, 2.7–2.6 g/cm³ and 2.6–2.5 g/cm³. The grains of each fraction were pulverized (to ~2 μm) and random oriented mounts were prepared for XRD analyses. Glass slides preparation was preceded by submitting the powdered samples to carbonate and divalent cations removal using acetate buffer and saturation with Ca followed by dialysis. Oriented slides were prepared only for separated <2 μm fraction. XRD analyses were performed with the use of Philips X'Pert diffractometer. The random mounts were scanned from 2–64° 2θ and the oriented mounts from 2–52° 2θ (in air-dry and after ethylene glycol treatment). For every sample the Ir index was measured (ŠRODON, 1984) and numerous computer simulations with the use of NEWMOD program were performed. During simulations lognormal crystallite size distributions (*N*= 4–10) were assumed. Fe³⁺ and K⁺ contents for glauconite were changed according to the EDS data obtained for single pellets. The different values of smectite *d*(001) were also applied according to SATO et al. (1992).

Random powder XRD patterns revealed that glauconitic grains of each sample represent the evolved and highly evolved stages of glauconitization (*sensu* ODIN & MATTER, 1981), i.e. end member of glauconite–smectite (GL–S) family. It suggests that in the structure of studied material the glauconite layers predominate. It is confirmed by diffraction patterns of oriented preparations. The air-dry and glycolated patterns of high and middle density fractions only slightly differ in the shape and the position of glauconite peaks which indicates highly glauconitic material. Nevertheless, all samples contain some admixture of expandable layers as evidenced by Ir index >1. On the patterns of low density fractions changes are larger.

Simulation in NEWMOD program allows us to precise identification of GL–S ratio and type of ordering. The estimated amount of GL layers in studied samples ranges from 86% to >95%. The GL/S ratio increases with increasing of the density of the glauconites, only samples of the lowest density fractions are characterized by smectite content higher than 10% and the R1 type of interstratification, the other samples exhibit the R3 type of ordering. The preliminary results we obtained clearly shows that the simulated patterns well correspond with the experimental ones. Thus, the computer simulations seem to be an effective method in determining the structure of GL–S. By applying this method some additional information to glauconite–smectite mineralogy may be added.

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Effect of bentonite compaction on the orientation of smectite particles

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An important function of bentonite as a buffer material in a geological disposal of high-level radioactive waste is to inhibit groundwater flow and to retard the movement of radionuclides in the region between the waste forms and surrounding rocks. It is well known from other studies that the diffusion of radio nuclides in bentonite is a function of various pore structural properties or parameters, such as porosity, dry density of bentonite, tortuosity, additives to bentonite, initial bentonite grain size, etc. Most of these parameters are directly connected to smectite particle orientation which may be influenced significantly during bentonite processing and compacting. This study is focused on the role of compaction on the orientation of smectite particles and/or crystals.

The effect of the clay particle orientation was tested directly or indirectly. Transmission electron microscopy of ultra thin sections observed at different magnifications was used as a direct approach. Indirect testing was performed using geotechnical methods.

Two types of Slovak bentonites were used for the study. The first, originated by the alteration of rhyolite tuffs, is composed mostly of Al-Mg-montmorillonite (65–70%). The second one is the alteration product of andesitic volcanism and composed of Fe-montmorillonite (55–60%). The bentonites were milled to the fractions <250, 45 and 15 μm and compacted to dry density between 1.6 g/cm^3 and 1.9 g/cm^3 . Two different compaction techniques were applied to bentonite samples: a standard uniaxial technique along with an isostatic technique with pressure up to 350 MPa.

Significant differences in orientation of particles were determined in samples depending on the type of pressure applied on samples and depending on their size fractions. Less important differences were identified between the bentonites of different origin. Difference in the orientation of particles has the implicit impact on the physico-chemical properties of compacted bentonite, which should be taken into account in construction of the long-term repositories using bentonite barriers.

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Effects of *in situ* biostimulation on iron mineral speciation in a sub-surface soil

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The *in situ* alteration of Fe redox states in subsurface soils by bacteria, otherwise known as bioreduction or biostimulation, may play a key role in the immobilization of hazardous redox active metals such as U, Tc, and Cr. The objective of this study was to characterize changes in Fe mineralogy occurring in a subsurface soil as a result of biostimulation, in order to evaluate the bioremediation potential of this approach. Biostimulation was achieved by injecting glucose into the soil through a small well next to a sampling well. Cores taken from the sampling well were analyzed by variable-temperature ⁵⁷Fe Mössbauer spectroscopy. Iron in the non-biostimulated soil was dominated by goethite (Fig. 1) with 0.12% Al substitution, mean crystallite diameter of 10.5 nm, and specific surface area of 133 m²/g. These properties were determined from the magnetic hyperfine fields, B_{hf} , at 77 K and 4 K using the methods of GOLDEN et al. (1979), MURAD & SCHWERTMANN (1983), and MURAD (1988). Results further revealed that biostimulation (Fig. 1) resulted in an overall loss of Fe from the system and major changes in the distribution of its oxide and oxyhydroxide mineral forms. Compared to the non-biostimulated soil, the spectral components assigned to goethite were appreciably diminished in intensity in the samples that had been biostimulated, whereas the hematite component was greatly increased. The Fe(II):Fe(III) ratio in the non-oxide phase (aluminosilicates) also increased, indicating that the bioreduction processes in the soil also affected the redox state of Fe in the constituent clay minerals.

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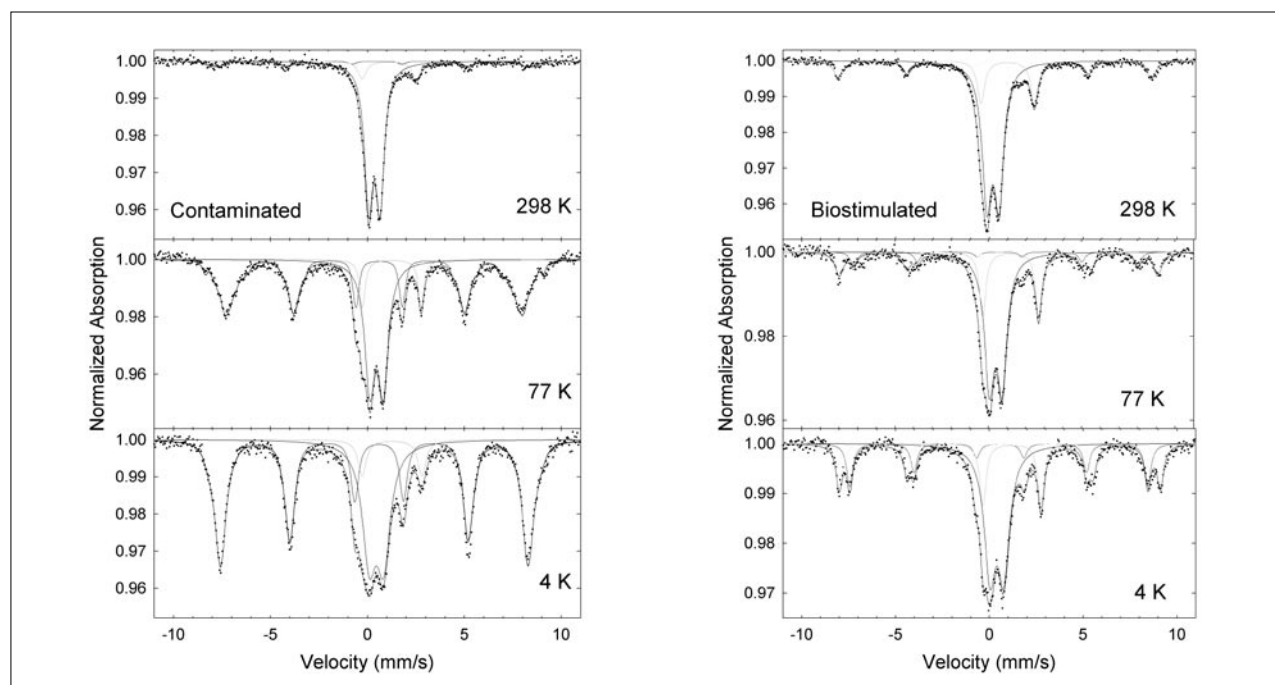


Fig. 1 Mössbauer spectra of non-biostimulated (left) and biostimulated (right) soils.

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Bacterial destruction of smectite and bacterial DNA bound in smectite-bearing sediments

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Knowledge of microbial numbers and activity in sediments is essential for understanding silicate biodestruction and clay/iron mineral bioformation in dependence on temperature and organic carbon sources. The aim of this work was to study the microbial activity of sediments in biodestruction of smectite and diatomite during microbial oxidation of organic matter which suppose biochemical transformation of sediments. Sediment cores were taken from two positions of Lake Baikal (Selenga Delta and Posolsky Bank). The concentrations of microorganisms found in the layers of Selenga Delta and in the Posolsky Bank are given in Table 1.

It was supposed that the attached bacteria were transported by the sedimentation of lake particles to the less favourable deep cold water of Lake Baikal. Selenga River is the largest tributary running into the Lake Baikal. The river suspension is richer in organic carbon during interglacial weathering and it can influence the concentration of bacteria and clay in sediments in the lake.

Non-cultivation based molecular methods, as polymerase chain reaction (PCR), are powerful techniques for complex microbial communities study in clay sediments. Isolation of PCR-ready DNA from sediments is difficult problem due to the presence of PCR inhibitors. From sediments, DNA was isolated using Soil DNA Isolation Kit and repurified with carboxyl group-containing magnetic nonporous poly(2-hydroxyethyl methacrylate-co-ethyl-

ene methacrylate) (P(HEMA-co-EDMA)) microspheres (D.Horak, Institute of Macromolecular Chemistry, CAS, Prague). The adsorbed DNA was released from the microspheres in a low ionic strength TE buffer. Psychrotrophic strains were identified in lake sediments using PCR by the primers BcFF2, BcAPP1, and BcAPR1. In the case of mesophilic strains one 284 bp PCR product was amplified, in the case of psychrotrophic strains two 160 bp and 284 bp PCR products were obtained. The results are given in Figure 1.

The experiments on smectite biodestruction were associated with extraction of Mg, Si and with microbial iron reduction. Destruction proceeded via association of live bacterial cells with smectite.

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Table 1 The concentration of microorganisms in the layers of Selenga Delta and in the Posolsky Bank.

Depth	Selenga Delta at 4°C	Posolsky Bank at 4°C
0–10 cm	730 cfu/g	470 cfu/g
10–20 cm	420 cfu/g	195 cfu/g
20–30 cm	32 cfu/g	70 cfu/g
30–40 cm	9 cfu/g	0
40–50 cm	49 cfu/g	0
50–54 cm	18 cfu/g	

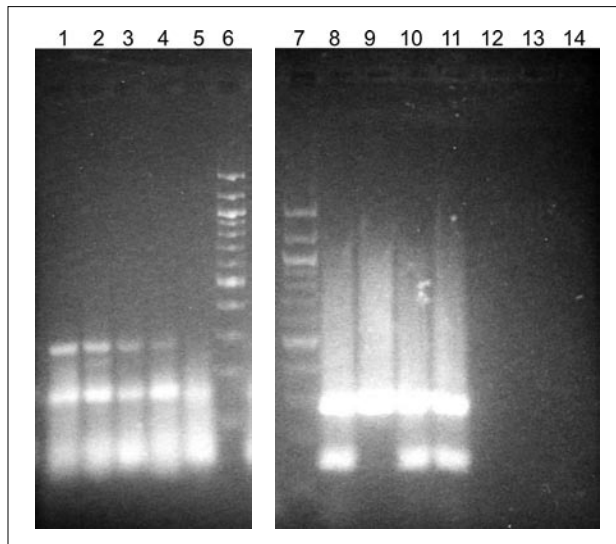


Fig. 1 Agarose gel electrophoresis of PCR products amplified from DNA isolated using magnetic microspheres. Conditions: 1.5 % agarose gel, TBE buffer (45 mM boric acid, 45 mM Tris-base, 1 mM EDTA, pH 8.0). Lanes 1–5: Selenga Delta samples from 0–10, 10–20, 20–30, 30–40, and 40–50 cm depths, respectively; lanes 6 and 7: DNA standard (100 bp ladder); lane 8: psychrotrophic *Bacillus cereus* CCM145 control DNA (10 ng); lane 9: mesophilic *B. thuringiensis* CCM197 control DNA (10 ng); lanes 10 and 11: psychrotrophic *B. mycooides* isolated from Baikal Lake sediments at 0–10 and 20–30 cm depth (10 ng); lane 12: negative control (water instead of DNA); lanes 13 and 14: DNA from Baikal Lake sediment samples (Selenga Delta, 0–10 cm) isolated using the kit or phenol extraction, respectively (without the step with magnetic microspheres).

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Bacterial removal of Fe(III) impurities from clay: A potential new technology

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Bioleaching is a technology applicable to iron removal from non-metallic raw materials. Improvement of non-metallics can involve the action of bacterial assimilatory or dissimilatory iron reduction.

The reduction of Fe³⁺ for the purpose of intracellular incorporation into protein is called assimilatory iron reduction. In contrast, dissimilatory iron reduction serves the generation of energy to fuel cell propagation (SCHRODER et al., 2003). Dissimilatory Fe reducing bacteria require mM concentration of Fe (LOVLEY, 1991), in contrast to assimilatory bacteria only require µM concentration of Fe (MAURICE et al., 2000).

Naturally occurring iron oxides are often coating the silicate surface of grains or are impregnated in the matrix in silicates of industrial importance. That is why they cannot be removed by electromagnetic separation. These Fe-rich impurities can be removed from industrial minerals such as kaolinite through biodissolution. This process involves a siliceous matrix, which is why silicate heterotrophic assimilatory bacteria of the genus *Bacillus* are of potential use in our experiments. Bioleaching resulted in a 17% decrease in Fe content of kaoline raw material from Rudník. Fe₂O₃ content decreased from 1.103% to 0.9128%.

The removal of oxidic Fe-phases from industrial silicates via bioleaching needs to be optimized with regard to the rate of iron reduction and dissolution in order to make the removal competitive against the chemical leaching. A new role for chelators as the low addition of AQDS or NTA during bacterial quality improvement of non-metallics, resulted in enhancing Fe(III) reduction or stimulating Fe dissolution under non-controlled anaerobic conditions. Our experiment showed that bacteria enhance Fe dissolu-

tion indirectly through microbially promoted pH changes and production of organic acids. AQDS stimulated bacterial iron reduction and Fe²⁺ concentration in solution was higher than Fe³⁺. However, NTA did not stimulate iron reduction but increased bacterial iron dissolution in form of Fe³⁺. The results presented in Table 1 showed that chelators might be added to iron-contaminated non-metallics during bioleaching processes for stimulation of rate of iron removal. The concentration of carbon source in medium is found to be crucial for the iron dissolution and metabolite production. Alternative cheap molasses and food-sugar have been used to optimize the cost of the bioleaching of iron on industrial scale. The low toxicity of chelators and bacterial metabolites (pH 4) makes bioleaching an attractive alternative way of quality improvement of non-metallics over chemical leaching (pH 2) which also improves quality of non-metallics but needs complex operation conditions and environmentally hazardous chemicals.

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Table 1 The highest concentration of iron in solution after 5–12 days bioleaching without and with chelators (AQDS – anthraquinone-2,6-disulfonate, NTA-nitritoltriacetic acid).

Organic source	without chelators		AQDS		NTA	
	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺
50 g/l food-sugars (after 5 days BL)	94.48	27.08	100.48	34.54	17.05	178.83
100 g/l food sugars (after 12 days BL)	134.46	36.76	180.9	53.22	81.45	195.45
Molasses (after 9 days BL)	106.54	93.8	154.26	100.35	50.5	219.26

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Clay minerals (I/S, kaolinite) in contact metamorphism related to Tertiary basalts intrusions in Lower Silesia (Poland)

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Clay minerals in sandstones subjected to contact metamorphism were studied. Samples of metamorphosed Triassic sandstone were collected in two quarries (Wilcza Góra and Krzeniów) in vicinity to Tertiary basalt intrusions in Lower Silesia (Poland). Non altered rocks were also collected for comparison. Optical microscopy, cathodoluminescence, scanning electron microscopy and X-ray diffraction were used.

Sanidine is the only high-temperature mineral determined in studied samples collected in close vicinity of basalt intrusion. Pelitic fraction of altered sandstones contains illite, illite/smectite (I/S) and mica. Ratio of smectite to illite in I/S minerals decreases with increasing distance from the contact. Further from the contact with basanite replacement of primary kaolinite (which is absent close to the contact) by illite was observed. In some samples fibrous illite was identified.

Close to the contact I/S contains about 10% of illite and 90% of smectite layers. With increasing distance amount of smectite decrease to 80% in 4.5–5 meters from the contact, and 75% of smectite in 10 meters distance. All identified I/S minerals from altered rocks are R0 ordered. First evidence of illitisation of kaolinite was observed at 8 meters distance from the contact. Initial stage of process is manifested by presence of potassium in margins of kaolinite crystals.

Primary clay minerals in sandstones are decomposed during contact metamorphism in the close vicinity to intrusion as it was described by BRAUCKMANN & FÜCHTBAUER (1983). They are replaced by newly formed minerals (I/S). Direct formation of I/S was probably related to high amount of iron and potassium in studied rocks (LANSON et al., 1996). Growth of fibrous illite (noted in samples collected at bigger distance from the contact) can be connected with hydrothermal growth (cf. BRUEL, 2000).

Variable amount of illite in I/S minerals can be explained in different ways: 1. different conditions of crystallization, 2. as an effect of different fluid flow in the sandstone layer;

i.e. WHITNEY & NORTHROP (1987) model, 3. lower temperature (retrogressive metamorphism?) growth (connected with second stage of hydrothermal activity?). The third process was well described by numerous authors (TÓMASSON & KRISTMANNSDÓTTIR, 1972; NIETO et al., 2005), both in case of contact metamorphism and hydrothermal activity. Growth of retrogressive minerals is connected with fluids of different chemical composition, temperature and pH.

Contact metamorphism caused decomposition of all clay minerals and formation of sanidine in high temperature zone in studied rocks. Subsequent hydrothermal activity (several stages?) resulted in formation of I/S minerals.

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Glauconitic materials from Lower Miocene Macelj Formation (NW Croatia) – new data

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The Macelj formation, situated in the northwestern part of Croatia, in the Hrvatsko Zagorje region, as well as in the adjacent eastern Slovenia, is composed of Vučji Jarek, Čemernica, Lipni Vrh and Vrbno members (AVANIĆ et al., 2005). The Vučji Jarek is the lowermost member of the Macelj formation laid transgressively on an erosional unconformity over Eggerian sediments. The Vučji Jarek sediments were deposited within a marine, nearshore environment under tidal influence. The sediments are characterized by horizontal-bedded and cross-bedded glaucony sandstones and tuffs. The Čemernica member succeeds the Vučji Jarek member. It consists of clayey and silty sediments affected by intensive bioturbation, and silty marls rich in ichnofossils. The deposits were formed in the offshore-transition zone between shoreface and offshore. The Macelj formation deposits were formed in Eggenburgian and in the earlier Ottnangian. The formation builds up an elongated syncline, plunging towards the east (ŠIMUNIĆ et al., 1995).

Glauconitic materials from Macelj-sandstones have been already investigated in detail (SLOVENEK et al., 1997; TADEJ et al., 1997) but during recent investigations glauconitic materials belonging to different members, Vučji Jarek and Čemernica, of the formation were investigated. Two samples of glauconitic materials were separated per member and investigated by X-ray powder diffraction (XRPD), infrared (IR) and Mössbauer spectroscopy, and by chemical methods.

Performed analyses revealed that investigated glauconitic materials from two members differ significantly. XRPD patterns showed that no impurities were present in investigated materials. Diffraction pattern of Čemernica samples have broader diffraction maxima, this is best seen for 001 peak, indicating higher expandable layer content. The observed $d_{(060)}$ for these samples of 1.510 Å in comparison to 1.516 Å for Vučji Jarek samples indicates higher Al content in them. In spite of the fact that IR spectra of all samples are characterized by poorly resolved broadened

bands, they differ in the appearance of the OH-stretching region. Those from Čemernica member samples have more pronounced band at 3603 cm^{-1} , which can be ascribed to Al–Mg cationic environment of the OH groups (BESSON & DRITS, 1997) in addition to bands at 3557 (Mg-Fe^{3+} and Al-Fe^{2+}) and 3530 cm^{-1} ($\text{Fe}^{3+}-\text{Fe}^{2+}$) that are practically the only visible in Vučji Jarek samples. In two samples from Vučji Jarek sediments potassium content (7.75 and 8.03 wt% K_2O) was higher than in two samples from Čemernica member having 5.58 and 6.24 wt% K_2O respectively, what is in accordance with observed differences in XRPD patterns. According to VELDE & ODIN (1975) the content of expandable layers in Vučji Jarek and Čemernica samples is approximately 5 and 20% respectively. Mössbauer spectra recorded at room temperature, fitted with four doublets with Lorentzian line shape, show differences in site populations for samples belonging to different members.

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Clay minerals as indicators of thermal history of Palaeozoic rocks from Marija Gorica Hills, NW Croatia

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In Marija Gorica Hills (NW Croatia) few outcrops of Upper Palaeozoic rocks can be found (ŠIKIĆ et al., 1979). According to these authors the rocks comprise different varieties of sediments. Having intention to determine thermal history of the rocks and to reveal possible metamorphic event the rocks have been studied by several complementary methods (polarizing microscopy, X-ray powder diffraction, and IR-spectroscopy).

Syn-deformationally grown quartz in a strain shadow around an elongate framboidal pyrite is a common microtextural feature for Marija Gorica sandstone. Strain fringes record deformation history in both their internal and external shape indicating a low temperature deformation (metamorphism). Distinct stages of deformation history are also preserved in slightly curved quartz fibres and the crenulation cleavage. At contact points in the quartz grains, effects of pressure solution are visible. These features inspired further thermal history study.

The illite "crystallinity" method, as one of the basic methods for evaluation of very-low grade metamorphism conditions in phyllosilicate bearing rocks was used following the recommendations of KISCH (1991). For the calibration purposes Kisch polished rocks standards were used. The obtained results expressed by Kübler index (KI) (KÜBLER, 1968) were in the range 0.33–0.38² CuK α indicating anchizonal, i.e. very low-grade metamorphism.

According to the results of XRD method minerals classified as kaolinite sub-group clay minerals were present in the investigated rocks. The transformation of kaolinite to dickite, two polytypes belonging to the sub-group, is temperature dependant according to EHRENBERG et

al. (1993). Therefore, in order to obtain information on thermal history of the rocks, polytype determination was performed. It was not possible to give unequivocal answer about polytype present by XRD method, therefore the <4 and <2 μm rock fractions were investigated by IR spectroscopy. Distinction between polytypes was based on spectrum appearance in OH-stretching region (EHRENBERG et al., 1993). The presence of illite made the determination of polytypes rather difficult. Nevertheless it was observed that kaolinite to dickite transformation was not complete, especially in fine grained rocks, i.e. rocks with lower permeability, in which kaolinite was the dominant polytype present.

Further research is planned in order to clear the eventual effects of various factors (bulk rock and fluid chemistries, etc.) having been responsible for the unusual persistence of kaolinite at relatively high (anchizonal) temperatures.

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Comparing surface charge heterogeneity of 1:1 with 2:1 type clay particles in aqueous suspension

Etelka TOMBÁ CZ and Márta SZEKERES

An analogous study to 2:1-type montmorillonite (TOMBÁ CZ & SZEKERES, 2004) was performed on 1:1 type kaolinite obtained from Zettlitz kaolin. Clay minerals are built up from silica tetrahedral (T) and alumina octahedral (O) layers. These lamellar particles have patch-wise surface heterogeneity, since different sites are localized on definite parts of particle surface (VAN OLPHEN, 1963). pH-dependent charges develop on the surface hydroxyls mainly at the edges, in addition to the permanent negative charges on silica basal plane caused by isomorphic substitutions (JOHNSTON & TOMBÁ CZ, 2002). Electric double layers (edl) with either constant charge density on T faces (silica basal planes) or constant potential at constant pH on edges and O faces (hydroxyl-terminated planes) form on patches. The local electrostatic field is determined by the crystal structure of clay particles, and influenced by the pH and dissolved electrolytes.

The acid-base titration of Na-kaolinite suspensions showed analogous feature to montmorillonite (TOMBÁ CZ et al., 2004). The initial pH of suspensions and the net proton surface excess vs. pH functions shifted to the lower pH with increasing ionic strength indicating the presence of permanent charges in both cases, but these shifts were smaller for kaolinite in accordance with its much lower layer charge density. The pH-dependent charge formation was similar, positive charges in the protonation reaction of (Si-O)Al-OH sites formed only at pHs below ~6–6.5, considered as point of zero net proton charge (PZNPC) of kaolinite particles (SCHROTH & SPOSITO, 1997). So, oppositely charged surface parts on both clay particles are only below this pH, therefore patch-wise charge heterogeneity exists under acidic conditions.

Electrophoretic mobility measurements, however, showed negative values for both clays over the whole range of pH showing the dominance of permanent charges, and only certain decrease in absolute values, much larger for kaolinite was observed with decreasing pH below pH~6.

The charge heterogeneity was supported by the pH-dependent properties of dilute and dense clay suspensions with different NaCl concentrations. Huge aggregates were

able to form only below pH~7 in kaolinite suspensions. Coagulation kinetics measurements at different pHs provided undisputable proofs for heterocoagulation of kaolinite particles. Similarly to montmorillonite, heterocoagulation at pH~4 occurred only above a threshold electrolyte concentration, which was much smaller than that for montmorillonite (only ~1 mmol l⁻¹ NaCl for kaolinite) due to the substantial difference in particle geometry. The electrolyte tolerance of both clay suspensions increased with increasing pH, pH~6–6.5 range was sensitive, and even a sudden change occurred above pH~6 in kaolinite. There was practically no difference in the critical coagulation concentration of kaolinite and montmorillonite (c.c.c. ~100 mmol l⁻¹ NaCl) measured in alkaline region, where homocoagulation of negatively charged lamellae takes place.

Rheological measurements showed shear thinning flow character and small thixotropy of suspensions at and above pH~6.7 proving the existence of repulsive interaction between uniformly charged particles in 0.01 M NaCl for both clays. The appearance of antithixotropy, the sudden increase in yield values, and also the formation of viscoelastic systems only at and below pH~6 verify the network formation due to attraction between oppositely charged parts of kaolinite particles. Under similar conditions the montmorillonite gels were thixotropic with significant elastic response.

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Two in one: two different glauconite series from the same rock, Sümeg Marl Formation, Lower Cretaceous, Bakony Mountains, Hungary

Erzsébet TÓTH and Tamás G. WEISZBURG

The Lower Cretaceous (Barremian–Early Aptian) Sümeg Marl Formation was described as a glauconite-bearing formation from the Bakony Mountains, Hungary (FÜLÖP, 1964). In the neighbourhood of Hárskút, the formation is built up of compact, sometimes nodular limestone layers alternating with loose marl beds. It is a little known formation because it has no natural outcrop and can only be studied in burrowed geological profiles due to the low durability of the marl beds. It formed in the inner part of a deep pelagic basin (HAAS, 2001). Our research focussed on the “glauconite grains” of the formation.

The white limestone sample has been crushed and decarbonated by 5% acetic acid. The insoluble residue (15 wt% of the bulk rock) was sieved and the >63 µm grain size fractions (6 wt%) were subjected to magnetic as well as density separation. These fractions contain detrital mica, greenish–yellowish chlorite, occasionally fibrous amphibole, feldspar (mainly albite), and metamorphic rock fragments of the same mineral constituents.

Additionally, *two series* of TOT layer silicates were identified: *a green grain series* covering almost the complete density region (>2.78–2.08 g/cm³) and *whitish–pale green, still magnetic biogenic cast*, in the lower density region (2.43–2.03 g/cm³). Due to the extremely small amounts of sample only part of the density fractions could be analysed for chemical (EPMA, SEM+EDX) and structural (XRD, IR) data on the studied layer silicates. Crystal chemical data are yet incomplete due to the lack of Fe²⁺/Fe³⁺ ratios.

In the *green grain series* yellowish green grains turn gradually into grass green and finally bluish green, glassy translucent grains with increasing density and magnetic susceptibility. They do not resemble traditional rounded glauconite grains and do not show any signs of primary biogenic substrate. Sometimes they are elongated and may exhibit colour zonation. They may be compact, pore-free, homogeneous, or porous and inhomogeneous. The grains may even exhibit some relic texture after an elongated mineral or a textured rock fragment. Concerning composition, they cover a continuous crystal chemical space from Fe containing dioctahedral Al-smectite over Fe containing illite and an IMA-non-defined region to glauconite–GG and finally to celadonite–CC (for suffixes see WEISZBURG et al., 2004). The tetrahedral Al-substitution is decreasing

with increasing density. The OH-stretching region of the IR spectra shows a broad shoulder around 3560 cm⁻¹ for the lower density fractions, while the denser grains (>2.78–2.68 g/cm³, of celadonite–CC and glauconite–GC composition) have well-defined, sharp (3602, 3557 and 3534 cm⁻¹) peaks, characteristic for the ordered octahedral sheet of celadonite–XC.

The *whitish casts* are unconsolidated, i.e. they can be smeared when wet. They fill foraminifer tests, gastropods/cephalopods, pores of echinoderm fragments. They may contain mineral inclusions (e.g. quartz, albite, TiO₂, apatite, chromite); have a pronounced spongy structure, with rounded, sometimes angular pores (3–15 µm in diameter). From thin sections it became evident that these pores were formed during dissolution of (partly euhedral; diagenetic?) calcite. A big portion of the grains, in spite of the whitish colour, is magnetic and may contain 10–17 wt% Fe₂O_{3tot}. These whitish casts form also a chemical evolution series, different from the green grain series: according to the increasing density iron rich dioctahedral Al-smectite (“nascent glauconite”) turns into glauconite–G0, with decreasing octahedral charge and slightly increasing tetrahedral Al-substitution.

These observations demonstrated the presence of two glauconitic series, different both in physical and chemical characteristics, within the same sediment.

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Mineralogy of glauconite-rich sand deposits in the Southern Slovakia

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Several glauconite-rich sand deposits are located in Slovak part of the Western Carpathians. They occur predominantly as green unconsolidated marine sands of Eggenburgian age in Cerova vrchovina Mts. (the Southern Slovakia). Some geological and technological explorations were performed in the area in the past. Because of low glauconite content (2–6%), the glauconite-rich sands are not used from glauconite point of view. The greensands are exploited only occasionally for local building and less demanding foundry purposes.

The main scope of the contribution is detailed mineralogical study of the greensands. Investigations were performed on whole rock, clay fraction and several fractions obtained by electromagnetic separation. The samples were studied by XRD, chemical analysis, electron microscopy and spectroscopic analyses (IR, Mössbauer and UV–VIS).

The green glauconite grains and pellets are present in the grain scale from 0.1 to 1 mm. Amount of magnetic fractions range from 4 to 8% of whole rock mass. The magnetic concentrates were obtained by electromagnetic separation of several fractions from 0.1 to 1 mm at current from 8–12 A. From 25 to 90% of glauconite in concentrates were determined by optical microscopy and XRD.

The amount of Fe_2O_3 in whole rock fraction varies from 2 to 5% while K_2O varies from 0.5 to 2%. The amount of

both significant oxides for glauconite identification increased in magnetic concentrate to about 20% of Fe_2O_3 and about 5% of K_2O .

Clay fractions contain dioctahedral mica (probably glauconite) and smectite as main clay minerals and trace amount of chlorite. Quartz, feldspars and clinoptilolite were observed as nonclay minerals in the fraction.

The first results of XRD quantitative mineral analysis by RockJock application (EBERL, 2003) showed that amount of glauconite is little bit more than 10% in some studied samples. The main mineral of glauconite-rich sand is quartz (60–70%). The other minerals are albite (8–9%), K-feldspars (4–6%), Fe-smectite (1.5–7.5%), muscovite (4%) and trace amounts of carbonates.

Our preliminary results confirmed previous works (review in ODOM, 1987) about mineralogical heterogeneity of greensands.

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Surface reactivity investigation of mechanochemically activated kaolinite

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The industrial application of kaolinite, an important industrial raw material (e.g. as additive in the paper, polymer and pharmaceutical industry) is closely related to its reactivity and surface properties. Very often kaolinites are mechanochemically ground to delaminate the mineral in order to increase its specific surface area. This kind of surface modification has a significant effect on the surface properties as well, due to the OH-group degradation in the kaolinite structure (FROST et al., 2001).

The reactivity of the kaolinite internal surfaces can be tested by intercalation, i.e. via the insertion of low molecular weight organic compounds (e.g. formamide or hydrazine) between the kaolinite layers consisting of the two-dimensional arrangement of tetrahedral and octahedral sheets (KRISTÓF et al., 1999; 2002). However, intercalation not only modifies the kaolinite internal surface through complexing via hydrogen bonding, but also results in a nanostructured mineral.

The nanocomplex thus formed can be investigated by the following instrumental techniques: thermal analysis (thermogravimetry, TGA; derivative thermogravimetry, DTG, controlled-rate thermal analysis, CRTA) coupled with mass spectrometry (TG-MS), X-ray diffraction (XRD) and diffuse reflectance Fourier-transform infrared spectrometry (DRIFT). Heating the sample in a thermoanalytical equipment can be considered as a kind of surface modifying process, as well. In this way mechanochemical activation (dry grinding), intercalation and thermal deintercalation *together* offer a technic capable of producing a so-called “superactive” surface of controllable properties. The treated surface contains different types of active sites of both acidic and basic character (HORVÁTH et al., 2005).

The physical and chemical nature of the active clay surface depends on the parameters of surface modification (e.g. grinding time, intercalating agent, as well as the conditions of heat treatment). With a systematic study of the effect of the treatment parameters on the surface properties of the clay, natural, environmentally friendly adsorbents with tailored surface properties can potentially be produced.

In the present work a detailed study of the adsorption properties of mechanochemically activated (ground, ground-and-intercalated) kaolinites is made using probe molecules as ammonia, pyridine and butane. These investigations are completed with specific surface area measurements, as well as stability and ageing tests.

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Iron oxides on Mars: their characterization from MER Mössbauer spectra

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A number of backscatter Mössbauer spectra (MS) acquired by the Mars Exploration Rover Spirit (MER-A) from targets at Gusev Crater, Columbia Hills, have been selected for characterization of the magnetic iron-bearing phases present in these targets. Non-processed sets of data, consisting of 512 channels of the 14.4 keV γ -ray backscatter counts for the rock target and an equal amount of channels for the corresponding transmission MS of the reference absorber, were downloaded from the web site <http://iacgu32.chemie.uni-Mainz.de/mer/>. The reference absorber is a mixture of α -Fe, α -Fe₂O₃ and Fe₃O₄. Spectra accumulated during successive sols (Martian days) for a given target and spanning a given temperature window ΔT , were added together. Summed target spectra and corresponding reference spectra that were both thought to be of reasonable statistical quality were then considered for further processing and interpretation.

The MER-MS are recorded using a triangular reference signal for the source motion, implying that they are composed of two complimentary halves. For a near-perfectly linear drive system (as in use in most laboratories), the two halves are mirror images with respect to a central, so-called folding channel. In that case, the two halves can be folded together and subsequent velocity calibration (velocity *versus* channel number) is then achieved from a (folded) spectrum of a reference absorber. The MIMOS spectrometers (KLINGELHÖFER et al., 2003) of the MERs' instrumental payload, however, exhibit a significant velocity non-linearity, making a laboratory-conventional folding/calibration processing of the raw MS data impossible. Earlier efforts to establish a workable folding/calibration procedure for the MER-MS are partly relying on the "drive error signal" of the MIMOS driving feed-back system (AGRESTI et al., 2006; DYAR et al., 2006). In the present work, an alternative approach in that respect has been developed. It is based on the adjusted peak positions of the eight most prominent lines of the calibration spectra and on the corresponding velocity values obtained for a proper mixture of α -Fe and α -Fe₂O₃ for which the MER acquisition sequences in the ten-Kelvin ΔT windows were mimicked in the lab.

The alternative calibration/pseudo-folding processing of raw MER data was successfully applied to the MS of the selected targets, being Clovis (four ΔT windows), Ebenezer-Cratchit (two ΔT windows), Ebenezer-Ratchit 2 (two ΔT windows), Woolly Patch (one ΔT window) and Uchben (three ΔT windows). Preliminary results derived from some of these MS have been reported earlier (KLINGELHÖFER et al., 2005). All spectra were found to be a superposition of five distinct components: (i) two relatively sharp sextets arising from antiferromagnetic and weakly ferromagnetic spin states of hematite, respectively, (ii) two sextets due to respectively octahedral and tetrahedral Fe species in magnetite, (iii) a hyperfine-field-distributed component attributable to goethite, (iv) a ferric doublet, and (v) a ferrous doublet. The two doublets are believed to be due to Fe-bearing silicates, either crystalline or amorphous. The spectral components of the magnetic iron oxides could be fit adequately imposing a minimum of constraints, and their adjusted parameter values are very consistent and generally perfectly in line with the parameters observed for laboratory oxide samples, implying that structure and morphology of the Martian Fe oxides are in essence no different from their terrestrial counterparts.

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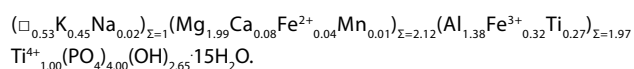
Mantienneite from Pinciná alginite deposit (Slovakia)

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Mantienneite is a phosphate mineral with idealized chemical formula $\text{KMg}_2\text{Al}_2\text{Ti}(\text{PO}_4)_4(\text{OH})_3 \cdot 15\text{H}_2\text{O}$. The first occurrence of this mineral was described from vivianite deposit of Anluoa, Cameroon. Associated with quartz, siderite and clay minerals (kaolinite, chlorite–montmorillonite mixed layer), mantienneite constitutes the matrix of sandy layers intercalated in black shales of lacustrine origin (FRANSOLET et al., 1984).

In our best knowledge, the mantienneite from Pinciná deposit is the second occurrence of this mineral in the world. It was found at the alginite deposit near Pinciná village (Slovakia). The alginite is the sedimentary rock rich in algal organic matter and clay minerals. It was deposited in a maar lake which was formed during the Upper Miocene basalt volcanic activity (Pontian). Alginite is a raw material useful in agriculture because of its specific facilities. It protects crops and trees against drought (water absorption capacity), traps nutrients in soil and many others.

The drill-hole samples of alginite were examined using XRD technique and total organic carbon (TOC) analyses. The rock matrix consists of quartz, smectite (nontronite), kaolinite, illite, plagioclase, chlorite, siderite and pyrite. Mantienneite was found as an accessory mineral only in some horizons where clay minerals are represented by dominating smectite and kaolinite, while illite is present in subordinate amounts. The TOC content in these horizons is exceptionally high and ranges from 4.97 to 9.41%. Mantienneite-bearing horizons are also enriched in secondary fissure-filling gypsum. Mantienneite forms well-developed spheres of radiating crystals (ca 200 μm in diameter) growing in clayey matrix (Fig. 1). Its chemical composition was determined by electron microprobe analyses. Average crystal-chemical formula calculated from 21 analyses on the basis of 4 (PO_4) is:



The M^{1+} position is occupied by K (0.12–0.92 apfu) with only negligible Na content. Considering M^{2+} site occupancy, mantienneite from Pinciná is almost pure Mg end-member. Its Mg content ranges between 1.91 and 2.27 apfu, which is much higher than in mantienneite from Anluoa (1.43 apfu; FRANSOLET et al., 1984). Al is dominant in M^{3+} site and its content is ranging from 1.06 to 1.87 apfu. The M^{4+} structural position is fully occupied with Ti, therefore its excess over 1 apfu is attributed to M^{3+} site.

Origin of mantienneite is probably related to fluid activity within sedimentary sequence containing alginite. Delicate habit of crystals suggests that this mineral precipitated probably directly from solution. The components required for mantienneite crystallization may have been mobilized by hot fluids during post-volcanic stage of maar evolution. The gradual decomposition of algal organic matter may have served as source of P, while other elements (Al, Mg, Fe and Ti) were probably released during alteration of basalt pyroclastics. Direct precipitation of mantienneite from solution is also supported by close association with secondary gypsum.

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Fig. 1 Mantienneite from Pinciná deposit.

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Mineralogy of fine-grained sediments related to karst phenomena in Villány Mts., SE Transdanubia, Hungary

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In the Villány Mts. various clay and silt sized sediments have been accumulated in connection with karstified Mesozoic limestones. Samples were collected from red clays filling fissures in limestone, fine clays deposited in the bottom of caves, partly produced by the ascent of thermal karst water, palaeosols and loess covering the surface of the limestone and lacustrine sediments of Upper Pannonian age deposited on the top of the limestone. The samples were collected from the limestone quarries at Beremend and Nagyharsány, as well as from various caves of the Villány Mts.

The grain size analysis has shown bimodal distribution, with maxima in the phi ranges 5–6 and 8–9, respectively. The proportion of the two maxima varies from sample to sample.

X-ray diffraction analysis was carried out on the bulk samples and on the <2 µm fraction. Essentially two types of mineral composition could be distinguished.

The first type is characterized by deeply weathered mineral assemblage consisting of mainly disordered clay minerals. The dominant components are disordered kaolinite, partly forming mixed layers with smectite, discrete smectite. Basal reflections are relatively weak. There is a few percent of gibbsite in most cases. Quartz is low or absent, cal-

cite is occasionally present. Normally both TiO₂ minerals, anatase and rutile are present. Iron is mostly represented by hematite, goethite is less frequent. The clay samples are of typical red colour.

The second type is a moderately weathered assemblage consisting of mainly well crystallized clay minerals. The dominant clay minerals are illite and chlorite, accompanied by mixed-layer illite/smectite, discrete smectite, kaolinite and occasionally vermiculite. The quartz contents are high, calcite is variable. Ti-minerals are much less frequent than in the first type. Iron is represented mainly by goethite while hematite is much less abundant.

The results indicate two main periods of clay formation. The first one may go back to the Upper Cretaceous tropical climate, the second one represent redeposited clastic sediments of the Upper Pliocene and Quaternary. The results are compared with data obtained earlier from the Beremend quarry and the surrounding, from the study of Upper Pannonian sequences of bore holes in neighbouring areas, as well as with data obtained from other red clay occurrences in south-eastern Transdanubia and the north Hungarian karst region.

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Continuous crystal chemical space for the dioctahedral iron-rich micas and related phases (celadonite, glauconite, Fe-illite)

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The dioctahedral iron-rich mica-related phases, the celadonite–glauconite group minerals (CGGM), have been defined and differentiated upon all of their possible crystal chemical positions, namely interlayer charge (IMA nomenclature, RIEDER et al., 1998), octahedral charge (AIPEA nomenclature, BAILEY, 1986) and tetrahedral charge (AIPEA nomenclature, BAILEY, 1980). The multitude of crystal chemistry based nomenclatures already forecasts that these minerals are difficult to distinguish on a crystallochemical basis. The routinely used formal identification methods (d_{060} and FTIR) do have strong limits.

CGGM have also been separated, from the second half of the 19th century on, on formation environment: celadonite was supposed to have magmatic, while glauconite sedimentary origin. However, data accumulating in the literature suggest that minerals of magmatic and sedimentary origin may have overlapping chemical composition.

For comparison the chemical data set (>350 analysis) we collected on CGGM, we started by building up a second database on all chemical data on CGGM available in the literature, with some outlook on their iron containing aluminous counterparts, too. At the moment, that second database contains more than 700 entries. Chemical data were filtered on the presence/absence of measured $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios and some crystal chemical constraints. The filtering process outlawed more than half of the data, leaving about 310 entries in the database for iron-rich dioctahedral micaceous phases. The valid(ated) data were plotted

into different graphical representation systems to check the crystal chemical range of these minerals.

We found that the crystal chemical space occupied by these minerals is continuous. The celadonite field of the IMA nomenclature is more populated towards the Fe^{3+} -rich side, while the glauconite field at lower interlayer charges is more populated on the Al-rich side. The transition towards the Al-rich regions is continuous in the low interlayer charge regions, pointing out the need for enlarging the IMA definition of illite.

These findings agree well with the predicted trend of glauconitisation: an Al–Mg-rich smectitic material is gradually turning into an Fe^{3+} –Mg-rich mica, where the charge consequence of the K uptake is compensated by the decrease of octahedral occupancy and by Al– Fe^{2+} substitution in the octahedral layer.

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Triassic red clays in Poland and their importance for ceramic industry

Piotr WYSZOMIRSKI

In the last years, the intense development of the Triassic red clays exploitation has been observed in Poland. It mainly takes place in central part of the country in the area of Świętokrzyskie voivodeship. Apart from Baranów deposit – that has been exploited since 1880 – the output of the red clays out of Chelsty (1993), Szkucin (1999), Pałęgi (2001) and Kozów (2004) has been undertaken. Moreover, the Gościńiec open pit will begin its activity this year. So, the current share of Triassic red clays in domestic output of clayey raw materials for heavy clay industry is high (more than 11%) at hardly 2% share in reserves. These raw materials are utilized in the Polish ceramic industry for the production not only heavy clay products (building bricks, roofing tiles) but also for making engineering bricks, among them wall and floor tiles. The latter are being produced by fast firing which needs great requirements concerning – among others – their mineral and chemical composition.

The mineral composition of studied Triassic red clays is similar. The clay minerals are represented by illite which is accompanied in varying amounts by kaolinite, smectite, chlorite and mixed layered minerals (mainly illite/smectite I/S). Non-clay minerals are quartz, hematite and sometimes – feldspars. Generally, the raw materials are free from undesirable phases, such as: carbonate minerals (calcite, dolomite), pyrite and water soluble sulphates.

In clayey raw materials for the production of ceramic tiles the special importance has the presence of organic matter. Its elevated share is the reason of undesirable black core in products. It is assumed that the organic matter content of green bodies for wall and floor tiles produced in single fast firing, expressed as elemental carbon, should be lower than 0.3 wt.% (de la TORRE et al., 1996). This content in Triassic red clays studied is distinctly lower (e.g. in the Chelsty clay the TOC amounts to 0.08 wt.%). The igni-

tion loss is also low (below 8 wt.%) which – with reference to non-calcareous clays – indicates the lack of organic matter (STEIN et al., 1980).

The clays studied show a good ability for sintering, most often at the temperature range 1100–1150°C. It is confirmed, among others, by the character of their firing curves (WYSZOMIRSKI, 2003; WYSZOMIRSKI et al., 2004), especially by very low (even <0.1 wt.%) water absorption. Phase composition of sintered clays can be revealed by the presence of quartz, hematite, the small amount of mullite and also by the amorphous phase. Such a composition is characteristic for the fired non-calcareous clays.

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Preliminary mineralogical characteristics of soils developed from Lower Triassic clay deposits (Buntsandstein) in the Holy Cross Mts. (S Poland)

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Soils developed from red clay deposits of different stratigraphic-facies units of the Lower Triassic (Buntsandstein) have been subject to investigations. Due to the specific character of the parent rock, it is difficult to determine the influence of pedogenic processes on the formation of the physical and chemical, as well as exploitation properties of these soils.

The study was focused on the mineralogical characteristics of the assemblage of clay minerals, allowing to determine the relation between the processes of litho- and pedogenesis during the formation of the soil substrate. XRD and SEM methods were applied in the analysis.

XRD studies pointed to the domination of illite or kaolinite in the soil substrate of the genetic horizons of all studied soils; these minerals are accompanied by a variable volume of chlorite or vermiculite. Detailed analysis of the diffractograms shows that features of these minerals are very similar to the features of minerals from the Triassic rocks lying beyond the influence of pedogenic processes. This testifies for a lithogenic origin of the minerals.

A low content of mixed-layer minerals e.g. illite-smectite type or vermiculite type HIV has been noted in the sub-surface ochric and mollic horizons. Their presence should be linked with the direct influence of the soil environment on the lithogenic soil substrate.

SEM analysis showed the variable structural properties of the clay substrate within the soil horizons. In the middle and lower part (below ca. 50 cm), structures built of intact packets of kaolinite or illite have been observed in pores between grains, as well as independent units. According to literature data they represent diagenetic structures typical of the Lower Triassic clay deposits (BARCZUK, 1979). In the surface horizons the structural features are strongly transformed towards dispersion, followed by secondary aggregation.

The obtained results indicate the dominance of lithogenic features of the soil substrate in the studied soils. Influence of pedogenic processes is restricted to the surface horizons and is reflected in physical destruction, whereas chemical influence leading to the transformation of minerals and formation of new pedogenic minerals is poorly marked. The poor development of pedogenic processes in the studied soils may result from their 'young' age (erosion of soil profiles) and from the distinctly large resistance of the clay soil substrate developed from Lower Triassic rocks to pedogenic factors.

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Mineralogy, Mössbauer characteristics and isotope age of Middle Riphean glauconites (the Olenek Uplift, Northern Siberia)

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K–Ar and Rb–Sr dates of globular glauconite correspond in many cases to early diagenesis of sediments and are close to their deposition age. Yet secondary chemical and structural alterations of this mineral can be accompanied by loss of radiogenic ⁴⁰Ar and ⁸⁷Sr and result in “rejuvenated” dates. The Mössbauer spectroscopy may be useful to detect such structural alterations. This paper provides the mineralogical and structural characteristics together with isotopic dates for Middle Riphean glauconites of the Arymas Formation of the Olenek Uplift. Chemical state and distribution of the iron atoms between non-equivalent crystallographic positions in glauconite structure are determined by the Mössbauer spectroscopy. The absorption signals of spectra were computer-fitted to six quadrupole doublets.

Based on the chemical composition of the glauconites, their structural formulae were determined. Then the proportions of the local cation arrangements of the Fe³⁺- and Fe²⁺-ions were calculated for both non-ordered and ordered distributions of octahedral cations. The structural studies of Fe-rich dioctahedral 2:1 layer silicates show that they are always trans-vacant (MANCEAU et al., 2001). The modeling is founded on the following concept of glauconite formation. It is supposed (GOROKHOV et al., 1995; CLAUER et al., 1992), that an unordered (“statistical”) distribution of the octahedral cations is typical of the new-formed glauconite. At this point atoms of the ⁴⁰Ar and ⁸⁷Sr inherited from a mineral-precursor do yet not leave glauconite structure. Only in the closing stages of its formation involving significant increase of potassium content, the cation ordering occurs in the octahedral layer, and a domain structure originates. The ordered distribution appears to result from a layer-by-layer dissolution–precipitation process. The redistribution of the cations in all glauconite layers should result in expulsion of radiogenic ⁴⁰Ar and ⁸⁷Sr alien to the mineral structure and in startup of the “radioactive clock”, based on decay of ⁴⁰K and ⁸⁷Rb. If such a glauconite is free of secondary alteration, its isotope date should correspond to the timing of early diagenesis, i.e. should be close to the stratigraphic age. This is best illustrated by glauconites of the Arymas Formation of the Olenek Uplift which Rb–Sr and K–Ar dates (1306–1318 and 1261 m.y.

respectively) correspond to the Middle Riphean age of the Arymas Formation.

As a result of the modeling, the proportions of local cation arrangements of the Fe³⁺ and Fe²⁺ ions were calculated for both unordered and ordered distributions of octahedral cations. These values were grouped and compared with the integrated intensities for corresponding quadrupole doublets in the Mössbauer spectra. Use of predicted values of individual quadrupole splitting from each type of cation arrangements of the Fe³⁺ and Fe²⁺ ions (DAINYAK et al., 2004) allows to calculate model values of quadrupole splitting for each doublet and to compare them to the Mössbauer spectroscopy data. The good agreement between theory and observation suggests that the chosen model of glauconite formation is a realistic one. Thus, the results obtained by the Mössbauer spectroscopy can be used as an evidence of the absence of secondary structural alteration of ancient glauconites and a criterion of stratigraphical significance of their Rb–Sr and K–Ar dates.

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Influence of the synthesis condition on Cu–Mn layered double hydroxides

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Layered double hydroxides (LDHs), known also as hydroxalcalite-like compounds or anionic clays, are characterized by the general formula $[M(II)_{1-x}M(III)_x(OH)_2]A^{n-}_{x/n}$ and can be easily prepared by coprecipitation. The structure of LDHs is very flexible and can accommodate within the layers a number of various M(II) and M(III) metal cations. The products of thermal decomposition of LDHs possess unique properties and are considered the most promising precursors of mixed oxide catalysts (VACCARI, 1999). On the other hand, Cu and Mn, due to their redox properties, especially important in electron transfer reactions, are known as active components of total oxidation catalysts. In view of this, our intention was to obtain Cu–Mn-based hydroxalcalite-like solids as precursors of mixed oxide systems for combustion of volatile organic compounds (VOCs), a process of immense importance for the protection of environment.

A series of Cu–Mn precursors were synthesized by the co-precipitation method at a constant pH, routinely used for the synthesis of LDHs of the general formula $[M(II)_{1-x}M(III)_x(OH)_2]A^{n-}_{x/n}$. Titration curves of aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ used in the synthesis experiments show that upon addition of the NaOH solution the precipitation of hydroxides is complete at pH values of ca. 6 and 9, respectively. In view of the reported observation that the co-precipitation frequently occurs at an intermediate pH value (CAVANI et al., 1991), the synthesis of mixed precursors was carried out at pH equal 6, 7, 8 or 9, by dropwise addition of aqueous solutions of

$Cu(NO_3)_2 \cdot 3H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ to the basic solution of sodium carbonate, using 1 M NaOH for pH control. Following previous reports (HANSEN & TAYLOR, 1991; GRYGAR et al., 2004; KOVANDA et al., 2005) it was expected that during synthesis carried out in air Mn(II) would oxidize and provide Mn(III) trivalent cation required for the formation of a hydroxalcalite structure. In an attempt to induce the hydroxalcalite structure formation some precursors were synthesised with the addition of Zn (replacing half of Cu), and/or Al (replacing half of Mn) nitrates. The XRD, XPS, BET methods, as well as chemical and thermal analyses have been applied for the physicochemical characterization of the samples.

The results revealed that the introduction of aluminium to the Cu–Mn system was the best way to induce the formation of an LDH-like structure, the appropriate adjustment of pH being the second factor determining the nature of the precipitate (Fig. 1).

At pH=6 a layered structure of basic copper nitrate $Cu_2(OH)_3(NO_3)$ as well as nitrate form of CuMnAl layered double hydroxide were observed. Increase of the pH of precipitation resulted in formation of carbonate CuMnAl layered double hydroxide. Simultaneously an increase of the material crystallinity was observed. With the increase of co-precipitation pH the amount of the manganese incorporated into the solids increased.

The work allowed for the optimisation of the synthetic procedure leading to active mixed oxide catalysts.

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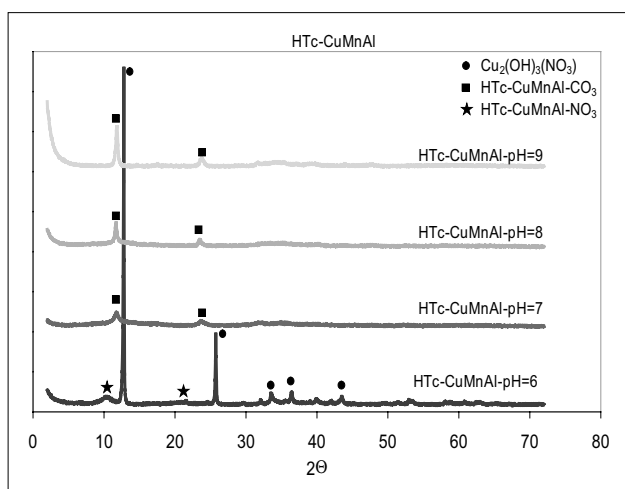


Fig. 1 XRD of CuMnAl layered double hydroxides.

Crystal-chemical factors affecting the distribution of octahedral cations over *cis*- and *trans*-sites in dioctahedral smectites

Bella B. ZVIAGINA

Dioctahedral 2:1 phyllosilicates may have different patterns in the octahedral cation distribution over the *cis*- and *trans*-sites. MERING & OBERLIN (1971) were the first to report *cis*-vacant (*cv*) structure for a sample of Wyoming montmorillonite. According to experimental data (TSIPURSKY & DRITS, 1984) beidellites and nontronites are *trans*-vacant, whereas montmorillonite and some Al-rich smectites, in which the layer negative charge is located in both octahedral and tetrahedral sheets of the 2:1 layers, are *cis*-vacant. However, several findings of *trans*-vacant (*tv*) montmorillonites have also been reported (e.g., DRITS et al., 2004). Some dioctahedral smectites consist of interstratified *cv* and *tv* layers although the information about the existence of such *tv-cv* smectites is very limited.

Crystal-chemical analysis of *tv* and *cv* dioctahedral smectites shows that the formation of *tv* and *cv* layers is related with the octahedral sheet composition and local order-disorder in the distribution of isomorphous cations. In the nontronite-beidellite series the main negative charge is located in the tetrahedral sheet, and the octahedral cations are mostly trivalent. Therefore a *tv* arrangement of these cations can provide local charge compensation for anions forming the octahedral sheet. The saturation of hydroxyl oxygens by positive charge is achieved by shortening R^{3+} -OH bonds due to displacements of adjacent OH groups towards each other along the *c*' axis. The saturation of oxygen anions shared by the octahedra and Al-bearing tetrahedra is provided by shortening of the non-bridging Al-O bonds. In contrast, from the local charge compensation point of

view, a *cv* octahedral sheet is preferable for Mg, Fe^{2+} -rich montmorillonites having random distribution of isomorphous cations, which implies the presence of R^{2+} -OH- R^{2+} arrangements. For such an arrangement in a *tv* sheet two adjacent OH groups are bonded with two R^{2+} cations; in a *cv* sheet, two adjacent OH groups are bonded with three octahedral cations, which provides more favourable conditions for local charge compensation. In contrast, Mg-bearing montmorillonite may be *trans*-vacant if the distribution of isomorphous cations is not random and octahedral Mg cations are dispersed to avoid Mg-OH-Mg arrangements.

The formation of *cv* layers is therefore favoured by relatively high contents of divalent octahedral cations in smectites with random octahedral cation distribution. The presence of only Al and/or Fe^{3+} in octahedra (nontronite-beidellite series) and dispersion of divalent octahedral cations in Mg-rich smectites are the factors that benefit the *tv* structure.

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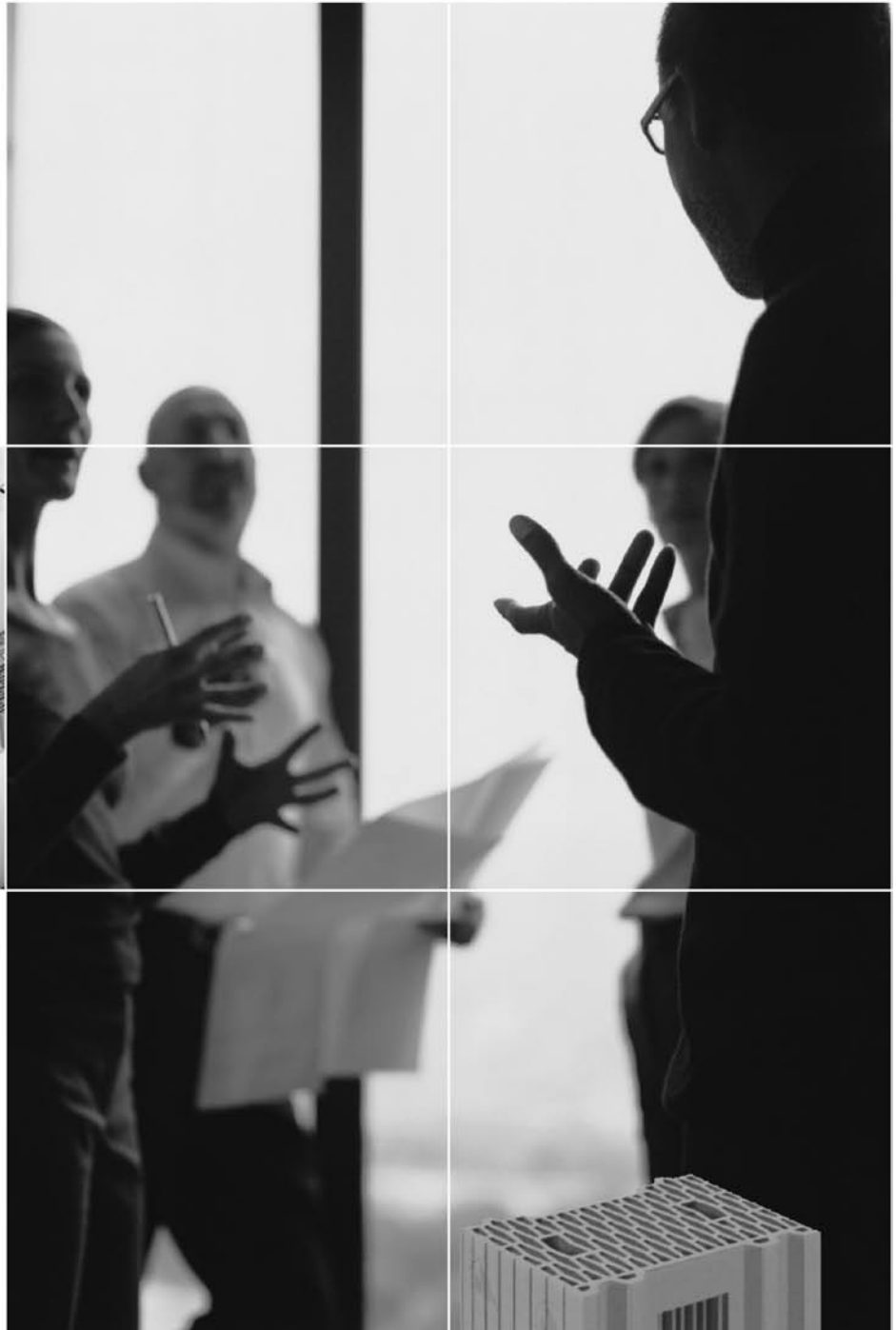
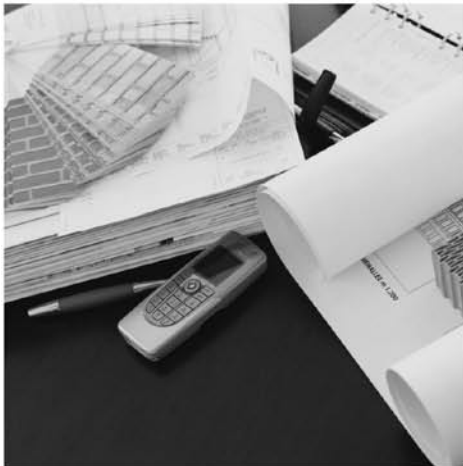
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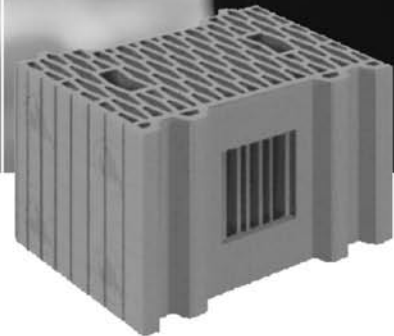
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