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FOREWORD

The Conference will be organized in the old mining town of Banská Štiavnica in Central Slovakia. The program will cover geological, mineralogical and chemical aspects of clays and zeolites in theoretical and experimental research and their applications in the industry and environment.

The main sessions will include Structure, crystallochemistry and particle size of clays, Chemical reactions of/on clays, Clays in sediments and soils, Hydrothermal clays and the Role of clays in the environment. A one day excursion will include visits to various clay deposits in Central Slovakia.

The Conference is organized by the Czech and Slovak National Clay Group; Faculty of Sciences, Comenius University; Institute of Inorganic Chemistry, Slovak Academy of Sciences and Town of Banská Štiavnica. The sponsorship of Novoker Lučenec, the leading Slovak wall tiles producer, is greatly appreciated.

About 100 participants will be hosted in the modern campus of the Forestry College in Banská Štiavnica.

The authors are responsible for both the scientific content and the English of their contributions.

The abstracts are ordered according to the first authors name.

Vladimír Šucha and Peter Komadel

HEAVY METAL RETARDATION IN SOME SLOVAK CLAYS AND CLAYEY SOILS

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Clays or clayey soils are often used as bottom liner for waste sites because of their stability against chemical attack, their low hydraulic conductivity and their ability to adsorb organic and inorganic pollutants. Several laboratory investigations on diffusion coefficients and retardation factors have been carried out on clays in the past ten years. However, there have been only very few field investigations on pollutants transport in clays. As laboratory investigations are limited in time, there is no possibility to investigate the long term transport of the pollutants. For several years it has thus been a wish of the authors to calibrate the laboratory measurements with field data.

In this field study the underground below three old waste sites in Slovakia has been studied in order to determine the "real" diffusion coefficients of important heavy metal ions under natural conditions. The waste sites had no engineered barrier but were situated in natural clay deposits. The retardation factor of several ions has been investigated also.

Samples were collected by rotary drillings through the waste sites. The drilling cores for chemical and mineralogical investigations were cleaned from the outer 2 cm, immediately cut in thin slices of about 0.5 cm, sealed in special sample containers and transported to the laboratory.

The laboratory investigations included the determination of the clay mineralogy, the carbonate and iron content, the cation exchange capacity, content of heavy metal ions and chloride. Larger pieces of drilling cores were used for hydraulic conductivity testing.

The study has shown that the heavy metal ion transport in clay by diffusion is extremely slow and that data from laboratory determinations of apparent diffusion coefficients correllate well with the data obtained from the field investigations.

In the Stupava waste site only Cu showed an slightly elevated concentration in the upper few cm of natural clay below the waste. Zn, Pb, Cr, and Ni concentrations were in the range of normal values. The chloride concentration was higher than normal till a depth of about 1 m. In Modra Pb, Cu, and Zn were concentrated in the upper 5 cm of the natural clay. Also here the Cl concentration was above normal till a depth of about 1 m. In B. Štiavnica the heavy metal ions were found in higher concentration in the upper 50 cm of the clay with a maximal Pb content of 15.3 g/kg about 10 cm below the waste. The investigation and the obtained data allowed the calculation of the diffusion coefficients and the retardation factor but also showed the difficulties in sample collecting by rotary drilling.

Table 1: Characteristics of the waste sites.

LOCALITY	WASTE SITE	
	age of site	**kind of waste**
Stupava	10 years	municipal waste, slack
Modra	18-20 years	municipal waste, demolition waste
B. Štiavnica	60-70 years	flotation residuals

LOCALITY	UNDERGROUND		
	age, genesis	**soil classification**	**k** (m/s)
Stupava	Neogen, sea water sediment	highly plastic clay	1×10^{-8} consolid.
Modra	Neogen, fresh water sediment	highly plastic clay	7×10^{-9} consolid.
B. Štiavnica	quartary clay	clay, sandy clay	6×10^{-9} triax.

Table 2: Characteristic of the clays.

LOCALITY	CEC (mval/100g)	CLAY CONTENT (%)			CARBONATE (%)	Fe_2O_3 (%)
		illite/smectite mixed layer	chlorite	kaolinite		
Stupava	19	40	5	3	20	
Modra	32	45	5	5	5	+
B. Štiavnica	25	40	5	5	0	4

TUFFITES OF THE CARPATHIAN NEOGENE FOREDEEP (UPPER EGGENBURGIAN - OTTNANGIAN, LOWER BADENIAN): MINERALOGY AND GEOCHEMISTRY

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Based on the composition of the clay fraction, Upper Eggenburgian tuffites have been divided into three groups: in the group **I** minerals of the smectite group prevail, micas including minerals of the illite group are represented to a lesser extent. In the group **II** minerals belonging to the group of smectite, illite and kaolinite are represented with a dominating position of kaolinite. The clay fraction of the group **III** contains kaolinite and a trace amount of illite only.

In the Lower Badenian tuffites the minerals of the smectite group prevail, in some samples micas are presented as well. Kaolinite and chlorite were not detected. In some samples zeolites are present, sometimes in high amounts. Mineral composition of the Badenian tuffites studied is most similar to the composition of the Eggenburgian tuffites-group I (with an exception of zeolite).

The Ca vs. Fe diagram divides Eggenburgian tuffites into two groups: group I includes tuffites with a low proportion of Fe (< 2 %) and belongs to the field of G type rhyolite (H-32, PMK-3, PMK-7), group II are tuffites from the drillings H-36, V-2 and V-14 which may be classified as rhyolites to rhyodacites with a high contents of Fe. A majority of the Badenian samples belong to the transitional type between G a W type rhyolites.

The Fe_2O_3 T + MgO vs. Al/Si or K/Na diagrams show that the closest affinity to the rhyolite composition is found in the tuffites from drillings H-32, PMK-3, PMK-7; the tuffites from drillings H-36, V-2, V-14 and PMK-6A are classified as rhyodacites to dacites. For the Badenian tuffites these diagrams commonly overlap with Badenian glasses and correspond to rhyolite, to rhyodacite tuffite from NP-902. The Rb vs. K diagram indicates that Eggenburgian and most Badenian tuffites contain material of acid (H-32, PMK-3, PMK-7, RO-1, HJ-1) up to intermediate character (H-36, V-14, NP 902, NP 905). The K/Rb ratios also separate these two types. The Ti/Nb vs.

SiO_2 plot show that all tuffites studied were belong to the orogenetic field close to the boundary with the anorogenetic area. In the Nb/Y vs. Zr/TiO_2 diagram the Eggenburgian tuffites and bentonites plot in the area of rhyodacites to dacites. Badenian tuffites belong to the field of rhyolites or on the boundary with rhyodacites. In the Y + Nb vs. Rb diagram the tuffites form a relatively homogeneous field corresponding to a single tectonic position, a volcanic arc. The samples from NP 902 and NP 905 drillings (low contents of Rb and high contents of Ba) differ from the other tuffites. The contents and distribution of rare earth elements show a depletion in light REE all tuffites and in heavy REE the Eggenburgian tuffites. The Badenian tuffites have a smoother REE profile with a distinct negative Eu-anomaly.

Although the Badenian tuffites form a relatively more homogeneous sequence than the Eggenburgian tuffites, based on geochemical criteria, some tuffites from NP 902 and NP 905 drillings can be distinguished from other Badenian tuffites.

EXTRACTION OF Cu(II) FROM BENTONITES BY ELECTRO-ULTRAFILTRATION METHOD

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The aim of this work was to find experimental conditions for the investigation of the bonds of Cu(II) cations on bentonite using the electro-ultrafiltration (EUF) method. The fine fractions of bentonites were saturated with 1 M $CuCl_2$, washed until negative Cl^- test, dried at 60 °C, and ground to pass a 0.2 mm sieve. 1 % suspensions of Cu-clays were analysed by EUF. The best results were achieved using the voltage of 200 V. To prevent the reduction of Cu(II) on the cathode, 0.3 M H_3BO_3 or 0.3 M H_3BO_3 + 0.001 M EDTA solutions were used. The results with 0.3 M H_3BO_3 showed insufficient complexing ability of this medium for Cu(II) — substantial portions of Cu were found on both the cathode and the cathode filter. On the other hand, the results in the 0.3 M H_3BO_3 + 0.001 M EDTA solution proved that the Cu contents on the cathode and on the ultrafilters were negligible. Two fractions of Cu(II) were identified in the samples, thus suggesting two kinds of bonds between Cu(II) and the clay. About 80 % of total Cu(II) in Cu-saturated Jelšový Potok bentonite were released within the first 40 minutes of the EUF experiment, while the last 20 % were bound more strongly to the clay and were released within the 40 to 105 minutes range. These results are promising for the further EUF analyses of bonds of other heavy metal cations in the clays and soils.

VANADIUM-DOPED TITANIA- PILLARED MONTMORILLONITE CLAY AS CATALYST FOR SELECTIVE CATALYTIC REDUCTION OF NO BY AMMONIA

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A series of V-doped titania-pillared clay catalysts, characterized by ICP AES chemical analysis, X-ray diffraction, BET surface area measurement and ESR spectroscopy have been tested in the selective catalytic reduction of NO by NH_3. Conversion of nitric oxide reaches 100 % over the most active sample. ESR analysis shows that vanadium dopant is anchored to the titania pillars. Vanadyl species of different degree of in-plane V-O π-covalent bonding are produced depending on the method of sample preparation. On increase of V content, polymeric vanadium species appear. Catalytic performance of these systems depends on the method of preparation and on the vanadium content. The best catalyst is obtained by exchange of pillared montmorillonite with vanadyl ions, to the extent of exchange below the level where a significant amount of polymeric vanadium species appears. The co-pillared catalysts, containing, according to ESR, vanadyl centres characterized by a higher degree of in-plane π-covalent bonding, perform worse than the exchanged samples.

MINERALOGICAL AND PETROGRAPHIC CHARACTERISTICS OF THE ZEOLITIC TUFFS FROM THE NW PART OF THE TRANSYLVANIA BASIN (RUMANIA) AND POSSIBILITIES OF USAGE

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Minerals belonging to the group of zeolites were mentioned in Rumania since the last century (1850–1870), as mineralogical and museum sample rarities.

Fine pyroclastic rocks — i.e. volcanic tuffs — represent stratigraphic markers for the Cenozoic deposits of the Transylvania Basin, the most important sedimentary basin in Rumania.

Among all the tuff horizons, the Dej Tuff (Lower Badenian) is the most representative, due both to its extent (thickness and area) and zeolitization processes, which affect the volcanic glass content. Petrographically, the volcanic tuffs are vitroclastic and vitrocrystaloclastic, of a rhyolitic and rhyodacitic nature. They represent the "failing" genetic type; subordinately, some "flowing" varieties occur.

The zeolitization process is a halmyrolitic one, beginning during syngenesis and being accomplished during diagenesis. Clinoptilolite — the Na-Ca variety — is almost exclusively represented; it is subordinatelly accompanied by chabasite and mordenite. Zeolitization is associated with smectitization of the volcanic glass as well, and sometimes with epigenetic carbonates formation.

The mineralogical characterization was performed by means of XRD, thermal analyses and electron microscopy.

Due to the high zeolitic content (30-80 % of the whole rock), the zeolitic tuffs from the NW part of the Transylvania Basin are exploited in quarries, the largest being at Mirsid, Salaj district) and processed in 8 granulometric classes (from 0.06 mm up to 5 mm). More than 30 fields in which zeolitic rocks are used are known, such as industry, agriculture, animal breeding and environmental protection.

THE CAMBISOILS ON VARIES PARENT ROCKS IN THE MTS. KRUŠNÉ HORY

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The mineral composition and heavy metal (HM) content of cambisoils were evaluated. The cambisoils occur on different rocks: gneiss, proluvial deposits, trachyte, rhyolite, pyroclastic deposits and basalts. The properties of topsoils and parent materials were compared. The sampling was carried out in dig profiles. Although all these cambisoils are the result of the same Recent soilforming process, their properties are different due to the parent rock.

Laboratory methodes: A grain size fraction less than 2 mm was used for all analysis. The quantitative mineral composition of soils was calculated using the results of XRD and silicate analysis. The trace heavy minerals were not determined because the amount of them is less than 1 %. The total content of the heavy metals Cd, Co, Cr, Cu, Ni, Pb, V and Zn was determinated using RFA, the extractable contents of them using 0.05 M EDTA and 2 M HNO_3 leaching.

Results: The mineral composition of all studied soils is similar: quartz (Q), feldspar (F), mica (Mi), kaolinite (Ka), montmorillonite (M) and vermiculite (V). However, the quantitative mineral composition of these soils depends on the type of parent rock.The succession of mineral quantity in soils from various rocks is the following:

Q:
proluvium > gneiss > rhyolite > pyroclastic deposits > trachyte
F:
trachyte > rhyolite > gneiss and proluvium > pyroclastic deposits
Mi:
proluvium > gneiss > rhyolite > trachyte and pyroclastic deposits
Ka:
pyroclastic deposits > trachyte and rhyolite gneiss > proluvium
Mo+V:
trachyte > gneiss > rhyolite > proluvium > pyroclastic deposits

The heavy metal contents are different in soils developed on various parent rocks. The highest total content of Co, Cr, Ni and V is characteristic for soils on basalt, both in the topsoil (Co 86 ppm, Cr 307 ppm, Ni 108 ppm, V 238 ppm) and the subsoil (Co 170 ppm, Cr 245 ppm, Ni 124 ppm, V 267 ppm). There is no significant difference between the total contents of other estimated heavy metals in soils on various parent rocks (Cu 15-56 ppm, Zn 68-100 ppm, As 10-47 ppm, Cd 0.3-1 ppm, Pb 12-80 ppm). The extractable contents (EDTA and 2 M HNO_3) are usually higher in topsoil than in subsoil.

DIAGENETIC MAFIC PHYLLOSILICATES IN THE GRAYWACKE FLYSCH DEPOSITS OF ŠAMBRON-KAMENICA ZONE (LEVOČSKÉ VRCHY MTS., EASTERN SLOVAKIA)

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Within the Upper Oligocene flysch formations of the Šambron-Kamenica Zone (northern margin of the Central Carpathian Paleogene, Levočské vrchy Mts.) sporadic occurrences of the graywackes—serpentinitic sandstones — have been recorded. The source material of sandstones (average modal composition $Q_{25}F_8L_{67}$) originated from disintegrated ophiolite series dragged upward along the collisional edge of the Centrocarpathian plate. Lithic grains consist mainly of serpentinites and palagonitized hyaloclastites ($Lq_{22}Lv_{62}Ls_{16}$). This composition gave rise to the production of specific type of mafic clay minerals during diagenesis.

Clay mineralogy was determined by XRD, SEM and EDS. Authigenic clay minerals of sandstone matrix are represented by trioctahedral smectite (saponite ?) and trioctahedral ordered (R1) mixed-layer chlorite/smectite (corrensite-like), which are sporadically accompanied with zeolites and calcite. Fractions < 2 μm usually contain trace amounts of serpentine group mineral, chlorite, and illite which are considered to be of detrital origin. Authigenic saponite forms coatings and rims (flakes perpendicular to grains) around detrital grains infilling intersticial pore voids. Formation of this type of clay matrix took place during shallow burial through replacement of fine-grained detrital lutum (protomatrix) by orthomatrix. Increasing depth of burial and local increasing activity of Mg and Fe ions in sedimentary fluids caused partial transformation of smectite to R1 chlorite/smectite. No intermediate random interstratifications have been observed. Direct precipitation of chlorite/smectite in relict pore voids, documented by typical honeycomb (cellular) textures, also took place (epimatrix). Main factor controlling chlorite/smectite formation was the availability of Mg, Fe ions. This presumption is supported by different saponite to chlorite/smectite ratio in individual sandstone beds with slightly different modal composition (palagonite/serpentinite clasts ratio).

SMECTITE TO ILLITE CONVERSION AS SEEN BY SEM AND TEM. A CASE WITH AMMONIUM INTERLAYER CATION

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Random and ordered mixed layer illite/smectite (I/S) with ammonium interlayer were identificated in the fossil hydrothermal system Harghita Bai (Eastern Carpathians). XRD analysis on below 2 µm fractions shows pure mixed layer ammonium illite/smectite (90 %, 40 %, 30 %, 20 %, 17 %, 8 % and 5 % smectite). SEM images of smectite exhibit a cornflake texture and at randomly I/S (80–70 % smectite) the edge of smectite can be seen relatively sharply. Ordered mixed layer I/S show a scalopped morphology with curled edges, and "ribbon crystals" of illite rise from plate. SEM images showed a well crystallized book of kaolinite crystal precursors substituted by illite.

TEM images show that the evolution morphologies change from flakey habit to lath habit during the transition from smectite to illite. We observed particles with characteristics veil which could be attributed to a smectite mineral phase, flakey particles in samples with rich random mixed layer I/S, more difuse or less organized fibres found along with the well developed previous morphology, lath fibres developed on smectite precursor minerals along one or more preferential directions and lath habit elongated along "a" direction (below 10 % smectite). Two generations of ammonium-illite have been distinguish. One generation well developed on smectite precursor minerals and the second generation formed on kaolinite precursor minerals. The polytype of illite is 1M. The type of interlayer cation does not influence the usual morphology in smectite to illite transition. Sometimes on lath-illite morphology could be seen the lattice fringe due that layers containing ammonium are easily destroyed by electron beam energy.

All this changed in morphology of mixed-layer I/S based on NH_4-fixation in the interlayer space of smectite and leading to a possible dissolution of smectite flakes. This chemical reaction is continuous, generates precipitation and growth of illite with lath morphology. The generation of illite formed on kaolinite precursor minerals could be generated in a solid-state transformation.

CLAY MINERALS IN THE INTERNAL FLYSCH OF THE EASTERN CARPATHIANS

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Clay minerals distribution in the internal flysch of the Eastern Carpathians has been studied by X-ray diffraction (XRD) and chemical analyses (EDAX/TEM). The samples investigated are turbidites, marls, clays and siltites from the Ceahlau and Teleajen Nappes. The clay minerals identified in the Sinaia Formation (lower, medium and upper members) — Ciuc Digit, Ceahlau Nappe — are composed of illitic materials (discrete illite, mixed layer illite/smectite, R = 3, -I/S-, mixed layer illite/paragonite -I/Pa- and discrete paragonite) and chlorite. Crystallinity values — Kubler index — (I_c) decreases from 0.7 to 0.38. Illite has a good crystallinity in the samples from the lower member and the average value of the I_c indicate that sediments are very close to the anchizone boundary (I_c = 0.38–0.4). The clay minerals assemblage with paragonite and mixed layer illite/paragonite appears only in medium and upper members but has not been identified in the lower member. I_c values are broader (0.5–0.7) in the samples provided of the medium and upper members due to the consistent presence of varying amounts of mixed layer I/Pa and discrete paragonite associated with illite peak. Towards the western part of the internal flysch (lower member of Sinaia Formation) the mineralogical assemblages and the I_c values indicate deep diagenetic conditions typical of anchimetamorphism. Discrete illite (mica) and paragonite component disappear with increasing diagenetic to anchimetamorphic conditions. In the Teleajen Nappe clay minerals have been studied in the Toroclej Formation, lower and upper curbicortical formation and Cotumba sandstone. The fractions below 2 µm are constituted of illite material (mixed layer illite/smectite, R = 2; R = 3; discrete illite, mixed layer illite/paragonite), chlorite, mixed layer chlorite/smectite and ± kaolinite. Kaolinite is present in small quantities (below 10 %). The crystallinity index measured on illite atested early diagenetic conditions. Expandability measured on mixed layer I/S is between 10–20 % smectite and is more comparable to the material from the Sinaia Formation (Ceahlau Nappe).

DEUTERIC ACTIVITY CONTRIBUTION IN THE GENESIS OF KAOLIN DEPOSIT OF SÃO VICENTE PEREIRA (PORTUGAL)

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Kaolin deposits of both residual and sedimentary type occur in Portugal. They are localized particularly at the north-western marginal zone of the Hisperic Massif. Residual kaolins result either from the alteration of a two-mica medium grain size granite or from alteration of gneiss and migmatite. Sedimentary kaolins occur generally in topographic depressions located nearby the residual kaolin deposits or in Quaternary fluvial terraces also close to the residual kaolin deposits.

The São Vicente kaolin deposit has been exploited for more than one hundred years by Vista Alegre, a porcelain plant known worldwide. The São Vicente de Pereira region is located on the northwestern border of the Ossa Morena Zone. The country rocks comprise gneiss, migmatite and tonalite gneisse (Medium Proterozoic) in the upper part and syncinematic Hercynian granite in the lower part. There is a structural control of post-magmatic events following preferently either regional alignments with attitude dominantly N40–50W or regional faulting with attitude dominantly N40–60E.

A two-stage hydrothermal activity evolved in the area. It produced a first sequence of greisenization events including an exogreisen system and in a later stage post-greisenization alteration. The late hydrothermal event is related to an easy and abundant circulation of pneumatolitic-hydrothermal solutions enriched in Si, B, F, Cl. As a result of that silicification, tourmalinization and fluoritization took place. Hydrothermal activity is connected with the progressive increase of H^+ metasomatism. A meteoric convective also system played a substantial role. With the additional input of meteoric waters a large amount of H^+ ions are consummed producing mineral assemblages which include clay minerals of the kaolin group (kaolinite and halloysite). Supergene alteration is superimposed on the late hydrothermal event.

PREDICTION OF CESIUM, STRONTIUM, RADIUM AND URANIUM ADSORPTION ON A FRESHWATER SEDIMENT MODEL

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The results of the bonding of cesium, strontium, radium and uranium to freshwater sediments are presented in terms of conditional adsorption constants by using a surface complexation model. The adsorption is considered to be a surface complexation process that is analogous to any ligand complexation reaction.

A relationship was found between the percentage adsorption, solid phase concentration and conditional adsorption constant value. Calculations based on a model sediment confirmed the potentially important role played by amorphous hydrated oxides of Fe and Mn, humic materials and clay minerals in the adsorption of Cs, Sr, Ra and U. The relative importance of the substrate depends on the precision with which the adsorption constants were found and knowledge of the exact sediment composition. Good agreement was found between the percentage adsorption values for real and model sediments.

It is stated that the toxicity depends mainly on the speciation of Cs, Sr, Ra and U in the system and not on their overall concentrations. It was found that at composition of sediment and concentration of tracer that usually are found in the river environment, both these materially alter the ability of the sediment to adsorb tracer. At high tracer concentrations, the adsorption is proportional to the tracer concentration up to a certain level (Henry's Law range). Above this range, the relative adsorption decreases with increasing tracer concentration. Increasing sediment load increases the total capacity to adsorb but proportionally less for each increment increase. Thus, the weight of tracer adsorbed per unit weight of sediment is higher for small concentrations of sediment than for larger concentrations.

From a knowledge of these factors, it is possible to predict for given sediment the amount of trace elements that will be taken up by a given weight on freshwater sediment in a very simple river system under equilibrium conditions. Prediction based on the values of the conditional adsorption constants are useful for test comparison with measured particulate/dissolved cesium, strontium, radium and uranium distributions in freshwater sediments.

INTERACTION OF METHYLENE BLUE WITH REDUCED CHARGE MONTMORILLONITE

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Li-reduced charge montmorillonites (RCMs) were prepared by heating of Li-montmorillonite at 100–210 °C. The interaction of RCM with methylene blue (MB) was studied by MB sorption, IR and VIS spectroscopies and XRD. Almost complete sorption of MB was observed on RCM when less MB than CEC of the clay was present. Equal or higher content of MB saturated the clay. The amount of adsorbed MB was almost unchanged with increasing MB/RCM ratio over the saturation point of sorption. The saturation point increased with the layer charge and was found to be by about 10–20 % higher than CEC for the expandable RCMs. RCM samples of the lowest layer charge, which contain collapsed, for MB cations inaccessible interlayer spaces, were saturated with amounts of MB approximately equal to CEC of the clay.

Impossibility of MB cations to penetrate into the interlayers of these samples was confirmed by unchanged d-spacings obtained from XRD. VIS spectra of the clay-dye suspensions provided qualitative aspects of the interaction of MB with the clay, such as MB di- and trimerization, and protonation of MB on the clay surface. MB adsorbed mostly in the form of trimers was identified in the water suspension of unheated Li-montmorillonite with MB (2.5×10^{-5} M, 1 mmol MB/1 g clay). On the other hand, suspensions of RCMs with slightly reduced layer charge (even by only about 10 %) contained more monomeric and protonated MB. This difference increased with higher charge reduction for all RCMs with expandable interlayers. The non-swelling RCMs did not form stable water suspensions and VIS spectra could not be measured. The observed changes in the VIS spectra of MB-RCM water suspensions reflect different properties of RCM suspensions as a consequence of lithium migration into the clay layers (induced acidification of clay) and/or layer charge reduction (changes in the swelling properties). Infrared spectra of MB-RCM intercalation compounds provided information on the form and the site of the MB molecules. RCMs of a high layer charge contained MB predominantly in the interlayer spaces, while those of the lowest layer charge adsorbed MB molecules on the external surfaces.

THE EFFECT OF SMECTITE COMPOSITION ON PEPTIDE BOND FORMATION CATALYSIS

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Clay catalysed glycine (gly) and diglycine (gly_2) oligomerization was studied in drying/wetting cycles at 80 °C. Two trioctahedral smectites (hectorite and saponite), three pure montmorillonites, a ferruginous smectite, a Fe(II)-rich smectite and three smectites containing goethite admixture were used as catalysts. Reaction products were analysed by HPLC.

Peptide bond formation on clays is a complex process including three parallel reactions: *1.* amino acid dimerization, *2.* cyclic anhydride formation, *3.* peptide chain elongation.

Glycine forms diglycine and diketopiperazine (DKP) (cyclic anhydride of glycine). The yields of DKP were several times higher than those of gly_2. DKP is formed by intramolecular condensation reaction from gly_2 and is favoured from thermodynamic and kinetic points of view. Therefore the yield of gly_2 did not exceed 1 % in any case.

The catalytic effect of smectites on gly reaction varies considerably. Peptide bond formation proceeds with highest yields on trioctahedral smectites. 7 % of gly is converted to gly_2 and DKP on hectorite after 7 days. In the case of dioctahedral smectites, highest yields were achieved using clays with a negative layer charge localized in the octahedral sheets (up to 2 %). The layer charge location probably controls amino acid zwitterion orientation at clay particle edges. Negative charge in the octahedral sheet enables the interaction of ammonium groups with octahedra and of carboxyl groups with SiO_4 tetrahedra. This interaction allows carboxyl group activation to form amino acid esters with -Si-OCO- bonds, which are activated intermediates for peptide bond formation. The presence of Fe(II) in dioctahedral smectites is reflected in a higher efficiency to catalyze amino acid dimerization (about 3.5 % yield after 7 days). Gly_2 forms DKP (main product) and higher oligopeptides (gly_3-gly_6). In comparison to gly_2 yields formed from glycine, peptide chain elongation starting from gly_2 proceeds more readily (1-4 % of gly_2 is converted to higher oligopeptides after 7 days). Peptide chain elongation (gly_2 reaction) proceeds not only as condensation reaction but also as reaction of DKP with amino acid (oligopeptide) by a molecular rearrangement mechanism (DKP ring-opening). The catalytic efficiency of clays do not vary so much in this case as in that of amino acid reaction. Nevertheless, most efficient are trioctahedral smectites and those with the layer charge localized on octahedrons, similar to amino acid dimerisation.

The findings, that peptide bond formation is catalyzed with highest efficiency on trioctahedral smectites and that Fe(II) enhances the yields of amino acid dimers, should be of considerable importance for prebiotic chemistry. Nowadays trioctahedral smectites, exhibiting the highest catalytic efficiency, are formed only in environments rich in magnesium, whereas on the primitive earth they were formed (under less oxidizing conditions) also by hydrothermal alteration of iron-rich volcanic and intrusive rocks. Moreover, such trioctahedral clays contained dominantly Fe(II) in octahedral sheets, whose effect on yield enhancement could be shown here.

THE CONTENTS OF CLAY MINERALS IN SEWAGE SLUDGE

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The work contains the results of an investigation of sewage sludge coming from a sewage-treatment plant in Lublin. The sludge was examined in its utilization aspect. Mineralogical and chemical examinations of the sludge were done. An X-ray diffractometer Geigerflex made by Rigaku Denki (Japan) with Co-Kα radiation (λ = 1.7889 Å) and filter Fe was used for mineralogical examination. Determination of the concentration of main components and trace elements in this sludge was done by X-ray fluorescence method with the use of XRF PW 1404 made by Philips (Holland).

The determined chemical composition showed that the sludge cannot be used for agricultural purpose due to high concentrations of heavy metals. This concerns especially Cd with concentrations in the range from 52 to 136 ppm and Ni with concentrations in the range from 78 to 132 ppm. It was found that up to 10 % of heavy metals were in water soluble forms. Metals present in this examined sewage sludge occurred in both mineral and organic matter.

The main components of mineral substance are: quartz, calcite, clay minerals and difficult to identify calcium phosphates. Among clay minerals illite, kaolinite and vermiculite were determined. The occurrence of organic-mineral mergers with the participation of clay minerals is also possible. Such preference is shown by illite which probably occurs in a few polytypical forms. The number of peaks on diffractograms taken from the sludge sample visible in the interval 10-11° 2θ Co-Kα proves this (Fig. 1).

The presence of illite and kaolinite in mixed-layers and with phosphates is possible. The increase of peak intensity for the sedimented sample specific for calcium phosphates seems to prove that.

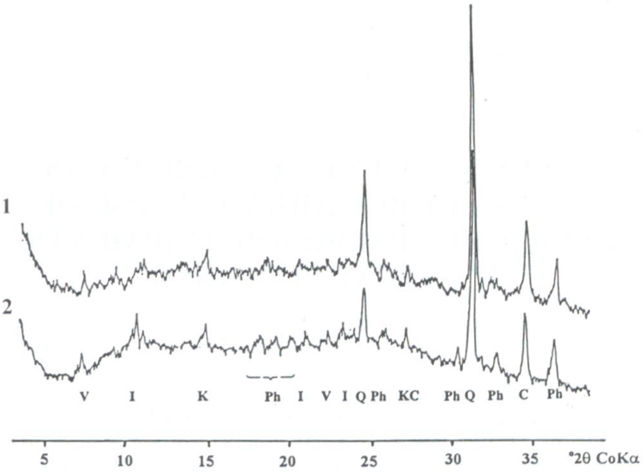

Fig. 1. Diffractograms of sewage sludge: 1 — dried sludge, 2 — sedimented sludge; C — calcite, I — illite, K — kaolinite, Ph — phosphate Ca, Q — quartz, V — vermiculite.

MOLECULAR SIMULATIONS OF THE MONTMORILLONITE STRUCTURE INTERCALATED WITH ALUMINIUM COMPLEX CATIONS

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Using Cerius^2 modelling environment the structure of montmorillonite intercalated with $[Al_{13}O_4(OH)_{24+x}(H_2O)_{12-x}]^{(7-x)+}$ cations, where x = 0, 2 and 4, has been studied. Present calculations showed, that the structure of the montmorillonite interlayer depends on the degree of hydrolysis of cations.

Modelling and minimization of non-bonded energies showed that the aluminium and oxygen planes perpendicular to the 3-fold axis in Al_{13}-cation (Keggin cation) are parallel with the silicate 2:1 layers. The values of basal spacings in the range 19.51-20.05 Å have been found depending on charge of the cations. Translation of Al_{13}-cations along the 2:1 layers gives only small fluctuation of the interlayer spacings. No preference for the position of Al_{13}-cations in the interlayer of monmorillonite was found during translation of those along the 2:1 layers. The main contribution to the binding energy between Al_{13}-cations and 2:1 layers comes from the electrostatic interactions.

Crystal Packer module in Cerius^2 modelling environment has been also used to study the structure of montmorillonite, intercalated with polymers of $Al(OH)_3$-fragments (gibbsite-like ring). Basal spacing for gibbsite-like polymers arranged in two layers in the interlayer varied in the range 19.54-20.10 Å in dependence on the type and arrangement of $Al(OH)_3$-fragments. The inhomogeneous distribution of intercalating species in the interlayer and consequently the turbostatic stacking of layers has been found for gibbsite-like polymers as well as in the case of Keggin cations. The dominating contribution to the total sublimation energy comes from electrostatic interactions for both intercalation species: gibbsite-like polymers and Keggin cations.

TRACE ELEMENTS AS INDICATORS OF THE SOURCE AREA AND AGE OF RELICT RED PALEOSOIL SEDIMENTS (CENTRAL SLOVAKIA)

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The geological structure of the central Slovakia is substantially influenced by the existence of central Slovak volcanic field. The adjacent areas (W, E, N, S) are often formed by sequences of Middle/Upper Triassic limestones and/or dolostones of the sub-Carpathian nappes. Relict red paleosoils or soil sediments are present in deeply karstified limestones and dolostones in the fissures widened by karst dissolution to different karst hollows. The aim of this work is to analyse the influence of the mainly Miocene stratovolcanoes of the central Slovak volcanic field on the origin of the relict red paleosoils in the karst infillings of Middle/Upper Triassic carbonates by means of trace element analysis. Therefore the trace elements whose distribution in clay sediments is affected first of all by the nature of parental rocks in source areas were studied. Vanadium, nickel and chromium are ranked among trace elements whose distribution is mostly affected by parental rocks in original source areas. The distribution of trace elements in Neogene clays redeposited from the central Slovak neovolcanics as well as from non-volcanic sources is well known (Kraus 1975; Kraus & Ďurkovič 1975). Trace element analysis of the relict red paleosoil sediments (distribution of Pb, Cu, Zr, Ti, V, Ni, Cr, Ba, Sr) and comparison of the results with the results of Kraus (1975) and Kraus & Ďurkovič (1975) have shown that the stratovolcanoes of the central Slovak volcanic field did not influence substantially the compositions of the relict red paleosoils from central Slovakia. During the Neogene volcanic activity different karst depressions were most probably already filled by the red paleosoils. The analysed red paleosoils are generally older than the Miocene volcanism.

NATURAL AND Al-PILLARED MONTMORILLONITES: EVALUATION OF THE MICROCRYSTALLITE THICKNESS

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Natural Ca-montmorillonite from Dimitrovgrad and its Al-pillared form were studied in TEM using SAED. TEM-micrographs of the natural montmorillonite show a typical morphology: "cloud-like" particles with diffuse outlines or flakes with curled edges, both with low diffraction contrast. After the pillaring the particles acquire more regular and subisomethrical shapes. It is observed a higher contrast, which is an indication for changes of their thickness.

The purpose of the study was to make a thickness assessment of the montmorillonite particles after the pillaring by analysis of the intensity changes of the diffraction maxima obtained in TEM.

Intensity curves of the montmorillonite and Al-pillared form were modeled by MULTYSLICE method, for the reflections obtained in the direction [001] of the electron beem, with a thickness increasing in the range from 0 to 40 nm. Structural models of the natural and pillared forms of montmorillonite (using our own and literature data) were the basis of the simulated microdiffractions. Average intensity curves of the reflections with equal d-spacings — (020) and (110) for the first diffraction circle, and (130) and (200) for the second one, were derived. Changes of the intensity ratios of the two diffraction maxima correlate with the microcrystallite thickness.

The thickness assessment has been done comparing theoretical and experimentally obtained intensity curves and an increase of the particle thickness of the Al-pillared form has been established.

HYDROTHERMAL SYNTHESIS OF Cs-Fe TRIOCTAHEDRAL FERRUGINOUS MICAS

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Cs-Fe trioctahedral ferruginous micas were synthesized under hydrothermal conditions at 100 MPa and either constant temperature (600–710 °C) or in a temperature gradient (10 °C/5 cm). Syntheses were conducted in sealed Ag tubes from standard oxide mixes. There was excess water in all runs, in some also an excess of CsOH solution. Oxygen fugacity during the experiments was imposed by the wall of the bomb, close to the NiO/Ni buffer.

The Cs analogue of annite grew as very fine-grained greenish coloured powder accompanied by variable quantities of pollucite and magnetite. The XRD powder pattern of Cs-annite was indexed on a 1M cell.

Under thermal gradient conditions, only Al-free Cs-ferriannite corresponding to the formula $Cs_{1.78}Fe^{2+}_{5.93}Fe^{3+}_{0.7}(Fe^{3+}_{1.80}Si_{6.15})O_{20}(OH)_{4.0}$ could be synthesized. Cs-ferriannite forms euhedral crystals brownish in colour. Cs-ferriannite is not only the mica with the largest unit cell, but its structure is quite relaxed and undistorted. This mica appears to be a stable crystalline phase that may serve for fixation and storage of radioactive isotopes of Cs in its interlayer.

LAYER SILICATES FROM RODINGITE BLACKWALL: A RECORD OF EARLY METASOMATIC PROCESSES (PRZEMIŁÓW, LOWER SILESIA, POLAND)

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A K-bearing chlorite-vermiculite intergradient mineral (as defined by Brindley 1980) and minute phlogopite inclusions were found in vesuvianite from the Przemiłów rodingite dyke and its blackwall, i.e. outer metasomatic zone formed at the expense of ultrabasic rock adjacent to rodingite and typically composed of Mg-rich chlorite as the dominant component.

According to X-ray oblique texture study (Wiewióra & Weiss 1985) the intermediate mineral represents Ia polytype, whereas a clinochlore from the same blackwall represents IIb modification like other chlorites from Lower Silesian rodingites and their blackwalls.

Determination of the intergradient mineral compositions (± chlorite intergrowths) on the basis of three tetrahedral Si cations displayed an almost complete range of charge variations from $O_{10}(OH)_2$ (mica & vermiculite) to $O_{10}(OH)_8$ (chlorite), as well as octahedral cation enrichment and $(Mg+Fe^{2+})$ increase.

The intermediate mineral seems to be a product of the phlogopite alteration (via vermiculitic stage). Its occurrence suggests that potassium was released from rodingite protolith during Ca-metasomatism accompanying low-temperature serpentinization. K^+-ions were subsequently consumed by phlogopite developed within the blackwall.

The study presents the use of blackwalls for revealing the origin and evolution of highly metasomatized rodingites and metarodingites. The blackwall can be a particular geological marker which can deliver information on the early events completely blurred by posterior serpentinization and alteration processes.

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IDENTIFICATION OF ILLITE/SMECTITE BY X-RAY POWDER DIFFRACTION TAKING INTO ACCOUNT THE LOGNORMAL DISTRIBUTION OF CRYSTAL THICKNESS

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The techniques for precise XRD identification of mixed-layer illite/smectite (I/S) developed by Środoń (1980) are based on the positions of chosen XRD reflections recorded for glycolated samples. The positions are affected by the proportion of component layers, the type and degree of ordering, the thickness of ethylene glycol interlayers and the thickness of mixed-layer crystals.

The method III of Środoń (1980) utilizes the position of two strong reflections migrating from about 15.4 to 17.4° and 26 to 27° 2θ. The diagram applies to the whole spectrum of I/S composition, random and ordered interstratifications and 16.6–17.2 Å thickness of ethylene glycol-smectite complex. The plot was constructed assuming three even distributions of crystal thickness: 1–8 and 1–14 layers per crystal for random, and 7–14 for ordered interstratification. These values cover the range of crystallite thicknesses which were considered reasonable for diagenetic illite/smectites. For random I/S, the measurements using two assumed distributions differ by 5 % S; for ordered I/S the error due to the selection of one arbitrary distribution could not be evaluated.

Recent studies of Eberl et al. (1990) and Drits et al. (submitted) demonstrate however, that autigenic illites and illites/smectites are characterized by a unique type of lognormal distribution of fundamental particles and crystal thicknesses.

The present work shows the result of modification of the original diagram (method III) of Środoń (1980) using lognormal distributions of crystal thickness and the estimates of the mean crystallite thicknesses (Tn — the mean number of layers in crystallites) for a given expandability (% S) determined using the experimental data of Drits et al. (submitted). The following numbers were used:

% S	100-20	15	10	5	2
T_n	5	6	8	13	20

The modification was carried out by calibrating the new diagram (based on the two reflections) using NEWMOD computer program (Reynolds 1985) for simulation of theoretical XRD (00*l*) patterns, adopted by R.C. Reynolds to accept selected lognormal distributions of crystal thickness as external files. The calculations were performed on the whole range of I/S composition (every 10 % S, and at the illite end — every 5 % S), assuming random interstratification (R0) in the interval 100 to 30 % S, R0.5—60 to 30 % S, R1—50 to 20 % S, R2—20 to 15 % S and R3—20 to 2 % S.

The comparison of the two identification diagrams (i.e. the one with even and the one with lognormal thickness distribution) reveals some important differences especially for the ordered interstratifications: in the range from 50 to 10 % S the differences account for about 3-5 % S error in I/S ratio estimations. In the case of random interstratification, the diagram based on lognormal distribution gives results similar to the values obtained for the 1-8 layers model of Środoń (1980).

The modified method has been tested in two ways:

1 — by comparing the estimated I/S ratio and thickness of ethylene glycol-smectite complex of experimental samples with the values obtained from the diagram based on the positions of two reflections in the range of 42-48° 2θ (which are not dependant on crystal thickness);

2 — by finding the best fit of experimental and NEWMOD patterns for the whole XRD profile, taking into account both the positions and the shapes of reflections.

TROUBLES WITH CRONSTEDTITE-1M

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The cronstedtite-1M is one of the twelve MDO polytypes (also standard or regular polytypes). It belongs, together with exceptionally rare $2M_1$ and relatively abundant 3T (polytype), to subfamily A, with the same stacking principle. The stacking in 1M is such that any stedtite layer is displaced relatively to the preceeding one by the same vector c_0-a/3; these layers in 3T are related by a 3-fold screw operation. But any single step in both polytypes is identical. It is, therefore, no wonder that these polytypes occur very often simultaneously within the same single crystal.

The first evidence on 1M was brought by Steadman & Nutall (1964) who found intergrowths of 3T and 1M, the latter manifesting itself by enhancing the intensities of certain characteristic polytype diffractions of 3T (these diffractions exactly coincide in both polytypes).

Bailey (1988) reporting about his own unpublished results mentions 3T crystals "having an apparent monoclinic symmetry ... perhaps as a result of twinning ...". This statement is consistent with that of Steadman & Nutall (1964).

Mikloš (1975) screened 30 cronstedtite crystals from various localities and labelled the specimen CR-8 from Eisleben (Saxony) as 1M, however, without an intelligible X-ray documentation.

Petrova (1989) and Fejdi (1990) claimed to have identified all cronstedtite crystals from Rožňava (Slovakia) as 1M. However, these works contain no diffraction photographs supporting this find and, moreover, two crystals from this locality, supplied for diffractometric studies, turned out to be 1T (Petříček, private communication).

Coey et al. (1989) claimed to have performed their measurements of electrical and magnetic properties of cronstedtite, using 1M polytype. However, they "identified" this polytype by indexing powder patterns of their specimens, and this is ambiguous: powder patterns of 3T, but even of disordered polytypes of the subfamily A might lead to the same conclusions.

A re-examination of the Mikloš's CR-8 crystal by precession method revealed that this is indeed an 1M polytype (diffraction evidence will be presented). The trouble is, however, that this crystal is so disordered that it cannot be used for a refinement of its structure.

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DETERMINATION OF ILLITE CRYSTAL THICKNESSES BY X-RAY DIFFRACTION

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Illite fundamental particles are the smallest separable particles of an illite. A knowledge of their thickness distribution permits calculation of specific surface area from XRD measurements. In past studies, the thicknesses of dispersed illite fundamental particles were measured by transmission electron microscopy (TEM) using Pt-shadowing, or by atomic force microscopy (AFM). These techniques are labor intensive, and may require more than a day to obtain accurate thickness distribution measurements for a single sample. Clay crystal thicknesses can be measured more efficiently using X-ray diffraction (XRD). Computer programs, such as "MudMaster", can extract crystallite thickness distributions from Fourier analysis of XRD peak shapes. The problem in applying this method to illites is that, in XRD mounts, illite fundamental particles often interact by swelling at particle interfaces, thereby leading to interparticle diffraction. Swelling effects may distort the shapes of illite XRD peaks, or, if undistorted, the peaks may give information about the thicknesses of MacEwan crystallites (i.e. stacks of crystals) rather than about the thicknesses of fundamental illite particles. The purpose of the present technique is to maximize X-ray scattering intensity without producing coherent scattering from adjacent fundamental particles.

The thicknesses of illite fundamental particles can be measured by XRD if Na-saturated particles are completely dispersed in aqueous solutions and mixed with aqueous solutions of polyvinylpyrrolidone (PVP) prior to XRD analysis. The polymer PVP separates the individual fundamental particles into oriented, discretely diffracting units. A typical XRD preparation uses 2 mg Na-clay dispersed in 1 ml distilled water mixed with 5 mg PVP (M.W. 1000) dissolved in 1 ml of distilled water. The suspension is dried in the range of 60-90 °C on a polished Si-wafer that has been cut perpendicular to (100). If particle dispersion is complete, the same mean illite fundamental particle thickness is found for all basal XRD reflections by Fourier analysis (in the MudMaster program), and the clay exhibits no tendency to swell, having basal reflections of 10 Å/n, where n is a whole number. Thicknesses measured by this method compared well with those made by TEM and other methods.

TRACING METALLIC CONTAMINANTS IN THE ENVIRONMENT. APPLICATION OF STEM/EDS MAPPING TO Cu-Zn SCALING

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The aim of the present work is a contribution to the knowledge of the speciation of trace metals (TM) in traceable fine fractions such as suspended matter, mud, dust. Pollution by heavy metals often originates from dispersed sources, its propagation is slow, and its long-term effects are difficult to predict without knowing the speciation of carriers and their behaviour with time. Better diagnoses of the sources and vectors of harmful substances can help to schedule monitoring of hazardous sitesand establish prognoses concerning the health, directly or through vectors such as water, plants, ...

The example presented here deals with cooling pipes of idustrial installations, which must be regularly cleaned from scaling with sulfuric acid. The suspended matter present in the cleaning waters of such installation has been collected and separated into two fractions: the sedimented fraction (heavy fraction) and the light fraction (floating fraction), at normal temperature and pressure in the laboratory. X-ray element mapping was carried out at a micrometric scale, using a Philips STEM 420 equiped with a Link AN10000 EDS system.

The sedimented fraction was embedded in resin and sectioned by ultramicrotomy. Element maps were acquired at a magnification of 4900. They correspond to rectangular areas of $12.2 \times 18.4\ \mu m^2$ digitalized in 64 by 64 raster images. This heavy fraction of the suspended matter is essentially calcareous and very poor in phyllosilicates. The elements Fe and Ca form separate phases. Cu is detected (1) — at low levels dispersed and associated with different elements, (2) — as tiny metallic grains of a few hundreds of nanometers.

The maps of the light fraction (of finer grain-size) were acquired at a magnification of 12,500 and represent areas of $4.8 \times 7.2\ \mu m^2$. This light fraction contains high levels of Cu but low Zn. Part of the mineral fraction consists in illitic phyllosilicates saturated with K and Ca. The rest is made of carbonates, phosphates, sulphates and accessory chlorides. Cu is strongly correlated to Ca, Na and S whereas Fe displays an indipendant behaviour.

Correlations between elements indicate an association of trace metals with organo-mineral phases in the light fraction. A large portion of the copper content is under easily mobile soluble form in this floating fraction. Abraded shavings present in the heavy fraction are also unstable in the supergene (oxidizing) physico-chemical conditions. It is concluded that filtering is unefficient to stop the migration of such pollutants. Our observations will thus help in (1) identifying the carriers (vectors) of contaminats; (2) tracing them in the environment; (3) predicting the future ways and means of migration and increase in metal content in soils and waters.

THE MINERALOGY OF SAPANCA LAKE SEDIMENTS AND ITS RELATION WITH GEOLOGY OF SURROUNDINGS

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The Sapanca Lake located in the Marmara Region, covers a surface area 47 km^2. It is a fresh water lake of elliptic shape, formed by an alluvial dam at a level of 30 m (above sea level). Sapanca Lake is located between two zones of the North Anatolian Fault. The southern and northern parts of the lake belong to the Sakarya Continent and Istanbul Zone. Therefore, the geological units on each side of the fault zone were originally different.

Three sediments types have been recognized for the deep sediments of Sapanca Lake, 1 — Sand, 2 — Silt and 3 — Clay.

The mineralogical investigations on the samples from the Sapanca Lake sediments include optical microscope and X-ray diffraction studies. On the other hand, clay fraction determination was realised these samples and then these fractions were analysed by X-ray diffraction method.

In general the mineral assemblage of the samples is: "quartz + feldspar + calcite + muscovite + chlorite + illite + smectite". The individual contents of minerals in the sediments have been estimated by X-ray modal analysis method with "standard addition". The albite type of feldspar, 2M1 and 3T types of muscovite, daphnite and/or aphrosiderite types of chlorite and dioctahedral type of smectite were identified by using these analytical methods.

Quartz, feldspar and muscovite have been observed as close-grained minerals optically. However, quartz and feldspar were also found as fine-grained materials, the mainly fine-grained minerals are clay and mica. Calcite was both free and lithic found in deep sediments.

ILLITIZATION OF ILLITE-SMECTITE IN THE JURASSIC AND PALEOGENE OF THE EASTERN BOHEMIAN MASSIF IN RELATION TO ORGANIC MATURATION AND THERMAL HISTORY

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The Jurassic and Paleogene formations of the south-eastern margin of the Bohemian Massif are important source rocks for oil and gas accumulated in the Vienna Basin and adjacent area of the Carpathian Flysch Belt. With a few exceptions they do not outcrop and are known exclusively from deep boreholes. Clay minerals and organic matter has been studied in these rocks to better understand the postdepositional processes such as compaction, dehydration, hydrocarbon generation and expulsion.

Diagenesis of clays in shales and marls is characterized by the smectite to illite conversion through the illite-smectite mixed-layer mineral series in close relation to bulk rock and clay composition. The Jurassic formation — Mikulov marl is of the Oxfordian to Tithonian age. It is enriched in carbonates and plagioclases and has little or no K-feldspar. The Paleogene shales — Těšany and Nesvačilka Fms. are of the Eocene to Oligocene age. They comprise less carbonates and more K-feldspar.

Illite-smectite is highly expandable and randomly interstratified to depth of 3-3.5 km in both formations. At about 3.5 km the transition to ordered IS (R1) occurs.

Organic maturation is manifested through increase of vitrinite reflectance and T_{max} of the Rock-Eval pyrolysis. Biomarkers (molecular fossils) show systematic changes in isomers of steranes, triterpanes, and tri-to-monoaromatic ratio.

Hydrocarbon generation and migration in the sedimentary basins is controlled by temperature and depth. Burial and thermal history of the Paleogene and Jurassic sedimentary formations are modelled using the "Pre-Drilling Intelligence" basin analysis software. The organic maturity and illite-smectite expandability data are used as calibration parameters to verify the models. They show that the Jurassic formation did not experience a significantly deeper burial than the Paleogene one. They were both exposed to the highest temperatures during the burial under the nappes of the West Carpathian Flysch Belt. This was a decisive evolution phase as most oil and gas was generated and expulsed during that time.

The above mentioned computer model simulates the smectite-to-illite conversion. The kinetic parameters of this reaction were modified using the trial and error method in order to get the best fit of the measured and simulated expandability data. These are compared with the kinetic parameters based on studies in the Neogene basins and give a better insight into the smectite-to-illite conversion in young and older basins.

A REINTERPRETATION OF THE ORIENTATION OF TRIMETHYLPHENYLAMMONIUM IN THE INTERLAYER SPACE OF SMECTITES

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The surface orientation of organic sorbates, such as trimethylphenylammonium (TMPA), onto 2 : 1 clays is commonly assumed to be such that the phenyl-N bond and the phenyl ring-plane are either both normal or both parallel to the 001 surface. We performed molecular dynamics simulations of TMPA sorbed to the surface of beidellite, which indicated that neither orientation is correct. The purpose of this study was to directly determine TMPA orientation on the surfaces of a variety of smectites using polarized infrared dichroic analysis (PIDA). Proper analysis requires (i) the formation of highly oriented organo-clay films, (ii) polarization of the incident infrared radiation, and (iii) measurement of the film about several angles with respect to the polarized electric field vector (EFV). Highly oriented films (3-4 µm thick, 2-3 mg/cm^2) were prepared by filtering (-0.7 MPa) suspensions (10 mg clay in 10 ml water or 20 ml of 0.1 M TMPA) onto 14 mm dia filters (0.025 µm) after removing excess TMPA. Polarized infrared measurements were taken with the films oriented at 0, 10, 20, 35, 50, and 57° with respect to the polarized EFV. Baseline subtractions were performed to account for the increasing sample thickness with respect to sample angle. The parallel orientation of the 001 surface was confirmed by the presence of birefringence bands in the IR spectra of untreated samples oriented at 0° and by the angular dependence of the Fe-O out-of-plane deformations (679 cm^{-1}) for TMPA-nontronites. The intensity of the 1460 cm^{-1} C-C stretch band (in-ring and normal to the phenyl-N) doubled and the intensity of the 1495 cm^{-1} band (in-ring and parallel to the phenyl-N) decreased. However, dichroic behaviour was not observed for the bands at 695 cm^{-1} (ring deformation) or 775 cm^{-1} (C-H out-of-ring-plane bending), both normal to the phenyl-N axis. Our PIDA results indicate that TMPA is oriented such that the phenyl-N bond is parallel to the 001 surface, and the phenyl ring-plane is within 20° of perpendicular to the 001 surface. The PIDA analyses are similar for several di-octahedral smectites, and reveal that predictions made by molecular dynamic simulations of organo-clay systems are representative.

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THE MINERALOGY OF FERRO-MANGANOUS SIALITES FROM MONEASA (RUMANIA)

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The Fe-Mn sialites from Moneasa are located in the Moneasa Mts., a well studied area as far as the geological, structural and ore deposit features are concerned.

The present paper brings new contributions concerning the mineralogy of Fe-Mn sialites, especially the clay minerals assemblage. The Fe-Mn minerals content varies both horizontally and with depth, the deposit being represented by high Fe-Mn, low Fe-Mn and without FeMn areas.

The mineralogical-petrographical studies show various textures and structures, starting from graywacke, rarely paratillites, to silty clays.

The lithoclasts are represented by intensely alterated rocks, such as rhyolites, dacites, porphyric dioritic andesites, metamorphic rocks and rarely, clays. The crystalloclasts are mainly represented by argillized feldspars, magmatic and metamorphic quartz and often, goethite pseudomorphs after pyrite. The matrix is argillaceous and displays variable Mn and Fe contents.

The clay minerals, represented by kaolinite, halloysite and illite can be grouped into two major assemblages:

1 — Fe-Mn minerals + kaolinite ± illite;
2 — halloysite ± kaolinite.

The absence of Fe-Mn minerals from the second assemblage demonstrates the role of pH in the dissolution and precipitation of Fe-Mn minerals.

Halloysite displays two distinct origins: a primary one, and secondary one resulting from halloysitization of kaolinite.

DETERMINATION OF LAYER-CHARGE HETEROGENEITIES IN SMECTITES OF I/S PHASES FROM K-FIXATION- AND ALKYL-AMMONIUM ION ORIENTATION STUDIES

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The < 0.2 μm-fractions of pelitic sediments from two drillings in the Molasse Zone of Upper Austria (Puchkirchen 1 and Geretsberg 1) were investigated to study the development of the mixed-layer mineral illite/smectite.

The X-ray diffraction patterns of the mixed-layer phases showed an increase of illite with depth. After chemical analysis of the < 0.2 μm samples, the structural formulas of the I/S were calculated. The compositions of the end-member illite and smectite for this series of I/S mixed-layer phases were determined by extrapolation of I/S compositions. The end-member interlayer charge for the smectite component (+0.58 per $O_{10} (OH)_2$) turned out to be higher than reported for typical smectites (+0.32 to 0.47) (Koester 1981).

It was assumed that the high +0.58 charge is the mean for a mixture of a higher and a lower charged component. To confirm this assumption the magnitude of the interlayer charge of the smectites was evaluated by two different indirect methods: alkylammonium ion orientation and K-fixation by wetting and drying.

For the alkylammonium method (Lagaly & Weiss 1969) the samples were saturated with alkylammonium chloride solutions of chain lengths n_c 5-18. The X-ray diffraction patterns indicate a three component system, consisting of high charged and low charged smectites and interlayered illite.

With K-fixation (Eberl et al. 1986), carried out by K-treatment and followed by 100 wetting and drying cycles, the presence of a high charged smectite component admixed with low charged smectite could be confirmed. The wetting and drying of the K-treated samples led to interlayer collapse of the high charged smectite component and to the production of illite layers stable against exchange by 0.1 N $SrCl_2$.

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STRUCTURAL INHERITANCE UNDER TRANSFORMATIONS OF LAYER SILICATES

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The similarity of composition, atomic motive and symmetry of layer surface, heterodesmic chemical bonds in clay minerals structures produce the formation of numerous polytypes and isomorphous modifications with various degrees of structural ordering. Wide distribution in the Earth's Crust, good absorption and exchanging properties of clay minerals are the reason for their active interaction with their environment. This permits us to consider them as perspective typomorphic indicators of their formation and transformation conditions. The stepwise transformations of all layer silicates carried out in different hydrothermal conditions were studied by the X-ray diffraction method. Crystallochemical models of all clay minerals transformations were divided into three groups according to the degree of structural inheritance. *1* — The transformations passing within the groups of layer silicates with the inheritance of their structure and chemical composition: hydromica (Md) to hydromica (1M), kaolinite (Md) to kaolinite (1Tc) etc. *2* — The transformations passing between the groups of layer silicates with the inheritance of structure and composition of octahedral layers: kaolinite (1Tc) to hydromica (1M), dickite (2M1) to hydromica (2M1), metahalloysite (Md) to hydromica (Md), kaolinite to disordered mixed-layered phase (mica-montmorillonite), kaolinite to ordered mixed-layered phase (mica-montmorillonite), serpentine (1M) to phlogopite (1M), berthierine (Md) to biotite (Md). 3 — The transformations passing between dioctahedral and trioctahedral structures with the exchanging of composition of layers and partial inheritance of their structures: glauconite (Md) to biotite (Md), kaolinite to serpentine, kaolinite to berthierine, montmorillonite to saponite. The presented examples of the transformations of clay minerals show the relation between the main classification criteria of layer silicates: transformations of silicates to alumosilicates, dioctahedral structures to trioctahedral, the changing of the type of layer transformations of polytypes, formation of the mixed-layer stocking and cation disordering. The examples also have crystallochemical and genetical significance.

REACTIONS OF ORGANIC COMPOUNDS IN THE MONTMORILLONITE INTERLAYERS

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Interaction of sodium and octadecylammonium montmorillonite Jelšový Potok (Na-JP, OD-JP, respectively) with methanolic solution of diacetoneacrylamide (DAA) gives in intercalation complex with various basal spacings. The largest basal spacing (d_{001} = 3.33 nm) was observed for the sample OD-JP/DAA. As it has been reported earlier (Hlavatý & Oya 1994), the alkyl chain length of the organic cation in exchangeable sites of montmorillonite is a limiting factor for interlayer space expansion. The difference between basal spacing of Na-JP and Na-JP/DAA is about 0.7 nm, reaching the maximum d_{001} value of 1.96 nm while the difference between OD-JP and OD-JP/DAA is more than 1.4 nm.

Na-JP/DAA and OD-JP/DAA samples were subjected to gamma-irradiation (10^4 Gy and 2×10^5 Gy) to initiate reactions of the intercalated organic componds. An additional swelling of the silicate structure was observed. In the case of OD-JP/DAA the additional expansion was about 0.5 nm while the basal spacing of Na-JP/DAA remained almost unchanged after gamma-irradiation. The additional swelling of OD-JP/DAA is related to the rearrangement of the interlayer sorbate and reaction products.

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GENETIC ASPECTS OF ZEOLITE ALTERATION WEST OF SKLENÉ TEPLICE (NW PART OF THE ŠTIAVNICA STRATOVOLCANO)

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Zeolitic alteration is developed primarily in autochthonous and reworked pumiceous rhyolite tuffs and epiclastic volcanic sandstones to fine breccias of the Late Sarmatian/Early Pannonian Jastrabá Formation, with a high proportion of glassy shards, pumice and fragments. In a lesser extent it has been observed also in glassy marginal breccias of extrusive domes and in andesitic pumice tuffs underlying the Jastrabá Formation. Zeolitic alterations are limited spatially to overburden and surroundings of rhyolite endogenous domes (shallow lacoliths), affected by a late stage hydrothermal phase leading to pervasive silicification and adularization and to the formation of irregular veinlets and breccias with adularia, quartz, chalcedony and jasper.

Zeolitic alteration shows a distinct zonal arrangement. Glassy margins of endogenous domes and tuffs next to contacts show a moderate temperature·assemblage mordenite-cristobalite-quartz-smectite ± clinoptilolite. More externally laying tuffs show lower temperature assemblage clinoptilolite-cristobalite-smectite-quartz, which grades with increasing distance from the contact into the smectite-quartz assemblage. The described zonality confirms the genetic link of zeolitization to rhyolite endogenous domes, namely to their late stage hydrothermal phase with relatively high pH fluids. Zeolitic alterations of the described type have not been observed along low temperature quartz/chalcedony veins at the outskirts of the Hodruša-Štiavnica epithermal system.

ZEOLITE TUFFS OF THE JASTRABÁ FORMATION — POSSIBILITIES FOR THEIR APPLICATION

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The Sarmatian-Pannonian Jastrabá Formation extending mainly on the SW margin of the Kremnické vrchy Mts. and on the NW of the Štiavnické vrchy Mts. consists chiefly of rhyolite extrusives and effusives and acidic volcanoclastics up to 150-300 m thick. It contains economic occurrences of clinoptilolite and mordenite formed during diagenesis of rhyolitic vitric tuffs in lacustrine and terrestrial environments and by contact effect of younger rhyolite bodies.

At the Kremnické vrchy Mts., Bartošova Lehôtka-Paseka zeolite deposit contains mordenite as well as clinoptilolite. The content of the predominant Na-K-Ca mordenite concentrating in contact zones with rhyolite bodies is 20-50 %.

Recently large occurrences of zeolites mainly clinoptilolite of possible economic value has been explored on the NW of the Štiavnické vrchy Mts. in the area of Sklené Teplice (spa). The Ca-K variety of clinoptilolite content varies from 10 to 60 %.

The appropriate technological properties of zeolite tuffs and some application tests have indicated the potential of their utilization: sorption of toxic cations Cd, Cs, Sr and Pb, purification of technical and waste water, gas adsorption and catalyst, enrichment in oxygen, soil amendment and in enviromental protection.

CRYSTAL STRUCTURE REFINEMENT AND TWINNING OF CRONSTEDTITE 2H$_2$

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Cronstedtite, $Fe^{2+}_4 Fe^{3+}_2 (OH)_8 (Si, Fe^{3+})_4O_{10}$ is trioctahedral 1 : 1 layer silicate. A specimen of its 2H$_2$ polytype from Wheal Maudlin, Cornwall, UK, has been studied by single crystal X-ray diffraction. The parameters of a hexagonal cell are: $a = 5.500(1)$, $c = 14.163(2)$ Å, $V = 371.08$ Å^3, space group $P6_3$, $Z = 1$ for given formula. Hilger & Watts diffractometer, graphite monochromatized MoKα radiation ($\lambda = 0.7107$ Å) were used to collect 2195 reflections of which 381 were independent and 338 of them observed.

Least square refinement based merely on the model of stacking sequence $| e_+ u_- |$ gave R-factor equal to 4.54 %, but the ditrigonalization angle of the tetrahedral ring was unusually small ($\alpha = +0.5°$) and temperature factor of basal oxygen atoms was extremely high ($U_{eq} = 10.5(9) \times 10^2$). Also the Fourier map revealed elongation of corresponding peaks in direction of the vector **a**.

After some trials, the structure was further refined as the superposition of two individuals of the merohedral twin. The twin operation is defined as $(\mathbf{a}_2, \mathbf{b}_2, \mathbf{c}_2) = (\mathbf{a}_1, \mathbf{b}_1, \mathbf{c}_1) \times \boldsymbol{P}_{1\rightarrow 2}$, where $(\mathbf{a}_1, \mathbf{b}_1, \mathbf{c}_1)$, $(\mathbf{a}_2, \mathbf{b}_2, \mathbf{c}_2)$ are lattice vectors of the first and second twin individuals repectively and $\boldsymbol{P}_{1\rightarrow 2}$ is the twinning matrix of value $(1\ 0\ 0\ /\ 1\ -\ 1\ 0\ /\ 0\ 0\ \underline{1})$. The used program package SDS (Petříček & Malý 1990; Petříček 1994) enables refinement of merohedral and pseudo-merohedral twins up to six individuals.

This refinement gave R = 3.11 % and the temperature factor of basal oxygen was substantially reduced ($U_{eq} = 3.1(3) \times 10^2$). The ditrigonalization angle is $\alpha = +12.1°$, average d(M1-A) = 2.106 Å, average octahedral edge e(M1) = 2.97 Å, octahedral flattening angle Ψ(M1) = 60.6°, counter-rotation angle δ(M1) = 0.7° (there is only one octahedral position M1). The parameters of the tetrahedra are: T1: d(T1-O) = 1.695 Å, e(T1) = 2.77 Å, d(T2) = 1.740 Å, e(T2) = 2.845 Å. Fe preferentially enters into T1, (Si : Fe ratio in T1 is 0.54 : 0.46), T2 is entirely occupied by Si. Surprisingly, T2 tetrahedron is somewhat larger than T1.

Although this structure model is substantially better than the "average model", some ambiguities remain. The unusual sizes of tetrahedra and the still remaining relatively high temperature factor of basal oxygen atoms indicate, that some further improvement of the structure model will be needed.

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MINERALOGICAL AND CHEMICAL COMPOSITION OF THE CLAY FRACTIONS OF BULGARIAN BENTONITES

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Fractions less than 2 μm of bentonite clays from four Bulgarian bentonite deposits were investigated. Mineralogical composition — phase and quantitative — was determined using RDA, IR-spectroscopy and TEM-study. All the fractions consist mainly of monmorillonite with admixtures of cristobalite varying from 5 to 30 %. The close association of the two minerals was studied by TEM. An oriented intergrowth of the cristobalite and montmorillonite crystallite have been proved.

Crystal chemical formulae of the monmorillonites were calculated after subtracting the impurities from the chemical analysis data. Mössbauer and EPR-spectroscopy were used to determine the Fe-presence in the samples.

Determination of the layer charge characteristics of the montmorillonites was carried out using the n-alkylammonium method. Cation exchange capacities — interlayer and total — were also estimated.

The relation between the crystal chemical properties and the layer charge characteristics of the studied monmorillonites have been discussed.

XRD PROFILE ANALYSIS OF INTERCALATED MONTMORILLONITES

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X-ray diffraction characterization of natural and intercalated montmorillonites is usually limited to the apparent d-spacings estimated from the peak maxima in the raw data. This can lead to the wrong interpretation of the measured data.

In case of X-ray diffraction, the interference function is modulated by instrumental factors (Lorentz-polarization factor, diffraction geometry) and physical factors (structure factor, surface roughness effect). These effects lead to distortions of diffraction profiles, depending on the diffraction angle and peak width FWHM. As a result, the diffraction profiles for structures with a large line broadening (FWHM > 1°) exhibit a significant peak shift ($\Delta 2\theta \sim 1.5$ Å) especially at low angles $2\theta \leq 10°$.

Present work deals with the detailed analysis of all these effects, their corrections and their consequences for the interpretation of diffraction patterns (possible incorrect determination of lattice parameters or incorrect structure model). The investigated materials were montmorillonites intercalated with hydroxy-Al polymers.

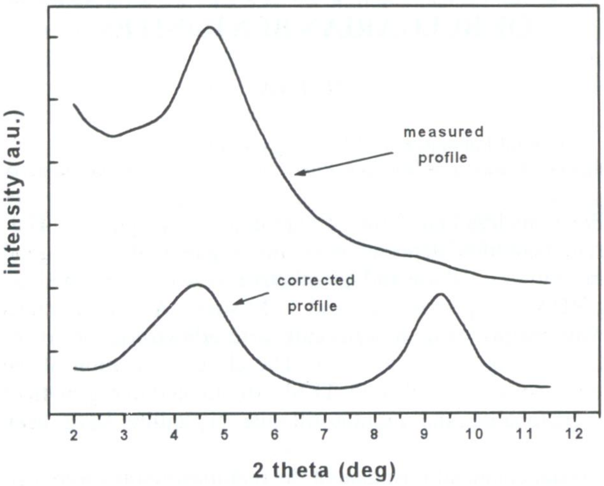

Fig. 1. Measured and corrected diffractogram of montmorillonite intercalated with hydroxy-Al polymers.

CHANGES IN THE LAYER CHARGE OF PROTON SATURATED SMECTITES DUE TO AUTOTRANSFORMATION

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H-forms of < 2 μm fractions of six bentonites of various Fe content were prepared by $H^+ \rightarrow OH^- \rightarrow H^+$ ion exchange with resins. H-smectites are known as unstable materials changing to their (H, Al, Fe, Mg)-forms with the progress of autotransformation. The changes in the acid sites and in the layer charge were monitored by potentiometric titrations and using the alkylammonium method, respectively. Potentiometric titration curves revealed that the number of strong acid sites varied among samples and accounted for 60-95 % of the total acidity in the freshly prepared H-forms. The number of strong acid sites decreased and that of the weak acid sites increased on ageing. The process of autotransformation in aqueous dispersion at 90 °C was completed within four days. Layer charge distributions of all samples were inhomogeneous with layer charges from 0.25 to 0.39 eq/unit $O_{10}(OH)_2$. Oxalate pre-treatment of the samples resulted in changes in the layer charge distribution due to the removal of readily soluble phases which may have blocked exchange sites. After autotransformation the alkylammonium exchange method revealed inhomogeneous charge density distributions; the fraction of layers of the highest charge were decreased. Comparison of total CEC (C_t, obtained from potentiometric curves) and interlamellar CEC (C_i, calculated from the mean layer charge) confirmed attack of protons from particle edges, however, for several samples the structural attack may also start from the interlayer space. Autotransformation of the H-smectites decreased the mean layer charge. Probably, protons attack preferentially the $Mg(O,OH)_{\overline{6}}$ octahedra during the autotransformation.

SLOVAK BENTONITES USED IN ENVIRONMENTAL STRUCTURES

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According to the multi-purposed performance of bentonites and their mixtures in the protection of the environment against pollution, the geotechnical and chemical evaluation of these materials is of great importance. The tests results of bentonites from localities Jelšový Potok, Kuzmice and Lastovce are presented and analyzed. Laboratory investigations have been performed in order to obtain a complete knowledge of the sealant quality of bentonite, zeolite, diatomite and some of their mixtures.

To measure the water adsorption capability of the materials the liquid limit tests were made for determining the water content of specimens at the boundary between the tested material's plastic and liquid states. The ability of specimens to adsorb water by measuring the increase in volume of water adsorbed by a mass of tested materials was ascertained by the Enslin tests. The measurements of specific surface area of the material crystal surface upon which water can potentionally be adsorbed were provided. The sorption of Cr, Cu, Mn, Pb and Zn by bentonite-zeolite and bentonite-diatomite mixtures was estimated by the flame absorption atomic spectrometry (Perkin- Elmer 1100).

The specimens were tested under the condition of confined compression. Hydraulic permeability measurements were performed in triaxial apparatus under different hydraulic gradient. Coefficient of permeability (k_v) of the specimens was determined. The triaxial k_v-values were compared with those of k_v-values from the compression test in the oedometer.

Based on tests results a number of specimens were compared. This comparison involved advantages and disadvantages of the each material. Due to these findings, it became possible to suggest the more effective application of each material. The above tests would serve to obtain sufficient information about mechanism of sealing process of bentonite and its mixtures. Thus a more accurate determining of their sealant quality could be evaluated. Conformable testing of sealing and sorption properties of such materials is not yet well defined.

The purpose of this contribution is to suggest the guide-line for verification of bentonite-based materials conformable with the design engineer's requirements for environmental sealants with low permeability acceptable in landfill construction for waste containment.

SURFACE-LAYER CHARGE AND HEAVY METAL ADSORPTION IN MICAS AND ILLITE/SMECTITE CLAYS: AN X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY

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Phyllosilicates, because of their layer structures, are ideal candidates for X-ray photoelectron spectroscopic studies of surface properties. XPS provides the opportunity to analyze quantitatively the outermost 2 : 1 layer of a mica crystal or clay mineral crystallite.

Utilizing as standards a well-characterized margarite, muscovite, and a fine-grain sericite, the electron escape depth, that is, the crystal depth above which analysis occurs, was measured as 15 Å. This makes it possible to analyze interlayer and surface ions on either side of the outer 2 : 1 layer and likewise to measure related surface charges on both surfaces of that layer.

For margarite and muscovite cleavage fragments the opposing surface charges were symmetrical as expected, but for the sericite the surface charge was asymmetrical, with a charge of -0.12 on the outer surface and -0.45 on the inner. That is, the outer surface was more smectite-like, in terms of surface layer charge.

Using the previous phyllosilicates as standards, the experiments were repeated for two high illite I/S clays (80 % illite) from the Vienna Basin and the Gulf Coast diagenetic sequences. The Vienna Basin I/S has a symmetrical surface charge distribution of -0.33 and the Gulf Coast I/S an asymmetrical distribution of -0.23 (surface) and -0.36 (internal). Thus the Gulf Coast illite, has a smectite-like surface layer, analogous to a MacEwan type crystallite.

Data will also be given to show how XPS can be used effectively to study selective adsorption of heavy metals on mica and clay mineral surfaces.

CLAY MINERALS IN SOILS DERIVED FROM VOLCANIC ROCKS IN SERBIA

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Six soil profiles on various volcanic rocks in Serbia were selected: basalt (Rudnik Mt.), andesite-basalt (Lake Bor, eastern Serbia), andesite (two profiles — Radan Mt.), latite (Kopaonik Mt.), and rhyodacite (Rudnik Mt.). The andesite-basalt is of Upper Cretaceous age, but the other rocks are of Tertiary age. Clay mineralogy was investigated using X-ray diffraction method. The soils over volcanic rocks are poorly developed (thickness 10-30 cm), and belong to rankers with A-C horizons.

The soil on basalt is an oxisol with A-B-C horizons. The main feature of all the studied soils is a mostly sandy composition (clay fraction up to 11 %). All the soils are more or less acidic in their pH values.

The soil formed from basalt contains in its clay fraction chlorite, illite, smectite, interstratified minerals (illite-smectite and chlorite-smectite), and Fe minerals. The soil clay fraction on andesite-basalt is characterized by the following composition: illite, chlorite, smectite and interstratified kaolinite-smectite. Clay minerals in soils derived from andesite are: I profile — illite and chlorite; II profile — chlorite, smectite, and illite. Soil derived from latite consists of the following clay minerals: illite, kaolinite, and smectite. Soil over rhyodacite is characterized by vermiculite, chlorite, illite, and smectite (in topsoil).

The weathering sequences of the primary rock-forming minerals and genesis of clay minerals are discussed.

MINERALOGY OF SOME HEALING MUDS AND CLAYS IN SERBIA

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There are many resorts with healing muds in Serbia. They are located in various parts of Serbia and are characterized by different geological settings. The purpose of this study is the determination of mineral composition of these muds and comparison of mineral and chemical composition with particular healing feature (treatment of rheumatism and other diseases).

Mineral composition of the healing mud from the Gamzigrad spa is: quartz, feldspar, calcite and clay minerals (illite, smectite, kaolinite). The healing mud from the Soko Banja spa contains calcite, quartz, feldspar and clay minerals (mostly smectite, illite and kaolinite are less abundant).

There are some healing clays on the Serbian market. Mineral composition of clay for internal use is the following: kaolinite, illite and illite-smectite. Clay for external use contains illite, kaolinite, and smectite. Another clay from the Belgrade area (clay of Miocene age) is used in external and internal manner. It consists of almost pure smectite.

The chemical composition and some physical features of healing muds and clays are discussed.

REACTIONS OF BENTONITE WITH DODECYL-BENZYL-DIMETHYL-AMMONIUM BROMIDE AND N-[1-(ETHOXYKARBONYL)PENTADECYL]-TRIMETHYLAMMONIUM BROMIDE

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Reactions of bentonite (Claire) with 0.2 M water solutions of dodecyl-benzyl-dimethylammonium bromide (A) and N-[1-(ethoxykarbonyl)pentadecyl]trimethylammonium bromide (B) were studied as model experiments for interactions of bentonite with solutions of detergents.

Reactions were carried out in the microwave field, at the laboratory temperature and at the boiling point of the reaction mixture. It was found that B only exchanges cations with host material completely at the laboratory temperature while A only in the microwave field or by prolonged boiling. Fully intercalated bentonite was also obtained by the interaction of 0.02 M solution of B. Basal spacings of the fully intercalated host material increased distinctly from 1.26 nm for bentonite to 3.20 nm for the intercalate of A and to 3.46 nm for the intercalate of B. DTA and gravimetric analysis showed that intercalate of bentonite and B contained 28 % of guest cation.

The change of intercalated cation to hydronium by boiling of the intercalate with 2 M HCl was not successful. At about 50 % of intercalated cation was released into solution, as was found by means of the titration by tetraphenylborate.

EFFECTS OF COPPER-COMPLEXATION AND ADSORPTION ON THE SURFACE OF MONTMORILLONITE

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Bentonite (from the locality of Istenmezeje, Hungary) containing Ca-montmorillonite was used for examining the effects of copper-complex forming and adsorption on the surface of montmorillonite. Bentonite was separated for getting a relatively pure material and only fraction under 2 μm was used to eliminate quartz and other large size minerals associated with montmorillonite. Exchangeable cation was replaced with ammonia (NH_3), thus a monoionic montmorillonite that shows adsorption of copper more significantly was examined.

In case of copper adsorbed by montmorillonite the d_{001} generally is about 12.5 Å. This distance can be changed by adsorption of water or hydrated copper depending on the amount of water bound to the mineral in different ways. Different kinds of adsorption isotherms proved to be practical for presenting adsorbed cation-amounts.

Copper forms complexes on mineral-surface with variable number of OH-ions. Different complexes have different stability, their precipitation occurs not at the same pH. In case of copper ion exchange (by isomorph substitution) occurs mostly at low pH (below 5.5).

The pH-dependence plays an important role in sorption. This explains why pH had to be kept stable at a constant level at each step. pH higher than 7 would be the best for observing the copper absorption because adsorption becomes 100 % around pH 7. Complex-forming of copper requires lower pH, at higher pH copper-hydroxides may precipitate. We chose pH 5-6 and 3, and used different concentrations of solutions of $CuSO_4$ from 0 to 1000 ppm.

The layer distances and half-widths of the X-ray diffraction reflections change depending on the amount of adsorbed cation and water. As to the X-ray diffraction line-profile analysis, the adsorption influences the crystallite size.

CHEMICAL STABILITY OF ORGANO-SMECTITES

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Ca^{2+} saturated < 2 μm fractions of three smectites of various Fe content (J, a montmorillonite from Jelšový Potok, Slovak Republic; S, a Fe-beidellite from Stebno, Czech Republic; and W, SWa-1 ferruginous smectite from Washington, USA) were treated at 60 °C for 3h with the solutions of salts containing organic cations M (tetramethylammonium) or D (dodecyl-tri-methylammonium) or O (octadecyltrimethylammonium). The amounts of these cations used were equal to 0.25, 0.50 and 1.00 mmol/g clay. This treatment led to Ca-organo-clays with increasing organic cations content in each series, as shown by the increasing intensity of the C-H deformation and stretching bands near 1480 and 2900 cm^{-1}, respectively. The organo-clays were further treated with HCl solutions to investigate their stability towards the acid attack. The mild acid treatments (0.1 M HCl, 20 °C, 3 h, $[H^+]$ = 1/3 CEC for all samples, and $[H^+]$ = 2/3 CEC for J) led to minor, undetectable changes in the FTIR spectra, thus proving negligible removal of both the organic and the structural cations from the clays. When an excess of protons (1.0 M HCl, 20 °C, 3 h, $[H^+]$ = 100 CEC for S) was used, substantial portion of M, but not of D and O, were removed from the interlamellar space but the clay layer resisted acid attack. This proves the lower stability of the M-clay, as compared to clays containing cations with more complex structure (D and O), in the acidic suspensions. The W clays were treated similarly to S, but at 95 °C. This treatment caused substantial dissolution of the octahedral layers of the Ca-clay and M-clays, as well as a complete removal of M cations from the M-clays. In contrast, much lower decomposition of the octahedral layers and minor removal of the organic cations was observed for D- and O-clays. This emphasises that the accessibility of the interlamellar regions is of considerable importance in determining the dissolution rate of smectites in hydrochloric acid. The hydrophobicity of these hybrid acid-treated organo-clays and the resulting affect on their catalytic activity has been assessed by studying the isomerisation of alpha-pinene which normally optimises when hydrophobicity of leached clays is a maximum.

ION EXCHANGE REACTIONS OF ZINC AND CADMIUM WITH Na-MONTMORILLONITE

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Ca-montmorillonite (Ca-MMT) from Ivančice was transformed on Na-montmorillonite (Na-MMT). Ion exchange reactions of Na-MMT with Zn^{2+} and Cd^{2+} ions present in chloride solutions were studied. For this study the batch equilibration technique was used. Exchange of Zn^{2+} and Cd^{2+} ions with Na^+ ion in Na-MMT were studied as a function of exchangeable ion concentrations. Equilibrium products of reactions were also studied using X-ray powder diffraction technique and maximum of non-symmetrical 001 profiles were determined. Very good correlation between amount of Zn or Cd ions captured in MMT equilibrium products and maximum of profiles when Zn and Cd concentrations increase the calculation of MMT profiles when Zn and Cd concentrations increase the calculation of MMT profiles was performed.

During the ion exchange reaction of Zn with Na-MMT the maximum of 001 profile (d_{001}) changed from 12.68 Å (for Na-MMT) to 14.89 Å (for Zn-MMT). In case of Cd the same value changed from 12.68 Å (for Na-MMT) to 14.91 Å (for Cd-MMT). Maximum amount of exchanged Zn was 0.45 mmol Zn/g Na-MMT and maximum amount of exchanged Cd was 0.42 mmol Cd/g Na-MMT. These "fully exchanged" products (Zn-MMT and Cd-MMT) were treated with distilled water (24 hours) to determine concentration of Zn and Cd in leachates. Analysis of leachates enabled us to conclude that only 1.6 rel. % of Zn and 2.1 rel. % of Cd from total amount of each of cations in Zn-MMT and Cd-MMT, respectively, were leached.

CLAY DIAGENESIS IN THE FLYSCH CARPATHIANS, SE POLAND

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Three deep wells: Paszowa-1, Kuzmina-1 and Cisowa-1, situated along a profile transsecting Skole Unit between Sanok and Przemyśl, penetrated up to 7 km of folded flysch sediments of Lower Cretaceous to Oligocene age, and the Miocene sediments of the foreland basin, upon which the flysch rocks were thrust. Bulk rock mineral composition and clay mineralogy of < 2 μm and < 0.2 μm grain-size fractions of core samples of shales and sandstones were studied by XRD, in order to recognize the pattern of clay diagenesis. The clay fractions were separated after removal of carbonates, organic matter and iron oxides from pulverized rocks, using standard Jackson (1975) techniques followed by dialysis. Mixed-layer illite/smectites were identified using the techniques of Środoń (1981, 1984). XRD investigations were complemented by SEM observations of sandstone samples.

In the three wells, due to folding and thrusting, the same lithostratigraphic units can be found at very different depths. Such situation allowed differentiation between the sedimentary and diagenetic variations in the clay mineral assemblage.

The major change of mineral compositon observed as a function of depth in all wells, both in shales and in sandstones, is illitization of smectite. % S is not sensitive to the age of sediments but only to their depth of burial. The pattern is identical in the three studied wells. Randomly interstratified 60 % S illite/smectite is present in shallowest shale samples. This composition does not change down to about 2 km depth (55 °C present day temperature), and then illitization begins. R1 interstratification is first encountered between 3.8 and 4.5 km (95 °C) and R3 clays — between 5.2 and 5.3 km (130 °C). The illitization curve is not smooth but quite scattered.

In sandstones down to about 4 km depth, illite/smectite composition is very scattered from almost pure smectite down to 35 % S R1 clay. On average, sandstone samples are more smectitic than shale samples. Below 4 km, an abrupt change takes place and the composition of illite/smectite in sandstones follows precisely the shale trend.

According to SEM observations, illite/smectite is present in sandstones as micron size, rounded aggregates. In the upper part of the profile, they also often contain calcite or pyrite. With depth, aggregates became pure clay but their morphology does not change. Calcite composition becames Mg, Mn and Fe rich. Below 5 km depth, authigenic quartz, albite and blade-shaped Fe-rich chlorite crystals were observed.

The abundance of kaolinite is not related to depth but is controlled by the lithostratigraphic units: kaolinite is most common in the Menilitowe Beds and Spaskie Beds. It is of detrital origin, occurring as micron-size aggregates mixed with iron hydroxides or pyrite (another mineral most abundant in Menilitowe and Spaskie Beds). Idiomorphic kaolinite crystals were not observed.

The shales of the Krosno Beds are characterized by a relatively low content of quartz and a high content of dolomite.

Smectite illitization profiles of the shales from the three wells are identical. % S isolines are horizontal, cutting folded strata from Miocene to Lower Cretaceous age. This pattern indicates that temperature and not age is the factor controlling the degree of illitization and that the present illitization profile has been established after folding and thrusting (in Kuzmina well, foredeep Miocene and overlying Lower Cretaceous flysh have the same diagenetic grade). Assuming the present geothermal gradient as representative for the period after thrusting and accepting the equilibrium model of smectite illitization curve it can be estimated that about 1 km of rocks has been removed by erosion from above the present erosional surface.

ACID DISSOLUTION OF REDUCED-CHARGE MONTMORILLONITE

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The effect of the swelling/non-swelling layer ratio on the dissolution of a series of reduced-charge montmorillonites (RCM) in hydrochloric acid was investigated by solution analyses, FTIR, XRD and HRTEM. Reduced-charge samples, prepared from the same parent Li-montmorillonite (Jelšový Potok, Slovakia) by heating at various temperatures (105-210 °C) for 24 h, were treated with 6 M HCl at 95 °C for periods up to 30 h. The analyses of both solutions and solid reaction products after HCl-dissolution showed that the dissolution rate decreased with increased amounts of Li fixed within the montmorillonite structure, i.e. with increased heating temperature. Differences in the acid dissolution process reflected that structural changes occurred within the RCM samples due presumably to different positions of fixed Li. The greatest extent of dissolution occurred for samples heated up to 120 °C, where Li was fixed only in the hexagonal holes of the tetrahedral layer. Slower dissolution of samples heated to 130 and 135 °C was connected with their lower swelling ability. These samples contained fixed Li in both the hexagonal holes of the tetrahedral layer and in the OLi (previously OH) groups. An increased amount of non-swelling layers in the samples prepared at higher temperatures (160 and 210 °C) caused their substantially slower decomposition in HCl. These two samples contained fixed Li in the hexagonal holes of the tetrahedral layer, in the OLi groups, and in the previously vacant octahedra. The calculated XRD patterns confirmed 20 % and 45 % pyrophyllite-like layers in the samples prepared at 135 and 160 °C, respectively. Mixed-layer pyrophyllite-like/smectite and pyrophyllite-like crystals, containing only non-swelling layers, were found in the sample prepared at 210 °C. The obtained results confirmed that the amount of swelling layers in RCM affects substantially their dissolution rate in HCl.

EFFECT OF THE SAMPLE HISTORY ON THE SWELLING OF REDUCED AND OXIDIZED SMECTITES

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Dioctahedral smectites of various Fe content (JP, Al-rich montmorillonite Jelšový Potok, Slovak Republic; H, Fe-rich montmorillonite Hroznětín, Czech Republic; S, Fe-rich beidellite Stebno, Czech Republic, and ferruginous smectite SWa-1, Washington, USA) were used to investigate the effect of organic cations TMA (tetramethylammonium), TMPA (trimethylphenylammonium) and HDTMA (hexadecyltrimethylammonium) on clay swelling as a function of Fe oxidation state. Investigating the *drying curve*, the clays were submitted to swelling pressure measurement at applied pressure without previous drying, while the *wetting curve* was obtained after freeze-drying the clays and then equilibrating them with 100 % relative humidity. Reduction of structural Fe in TMPA-exchanged smectites had little or no effect on swelling of JP, H and S along the *drying curve* at 3 atm applied pressure, but iron reduction increased the swellability of SWa-1 at both 3 and 0.1 atm. The swelling of SWa-1 decreased with increasing complexity of the interlayer cation along both the wetting or the drying curves in the order Na > TMA > TMPA > HDTMA, regardless of the oxidation state of structural Fe. Decreasing the hydration energy of the interlayer cation decreases swelling. However, iron reduction decreased the swellability along the *wetting curve*, which is opposite the effect along the *drying curve*. The number of collapsed layers in reduced Na-smectite increases with Fe reduction, but surfaces of uncollapsed layers hydrate more strongly than in the oxidized state. Organic cations disrupt the layer collapse mechanism in reduced smectites, thus allowing more of the strongly hydrating surfaces to participate in swelling. The freeze-drying of organic-cation exchanged smectites dehydrates the interlayer, which then resists rewetting.

THE THERMAL BEHAVIOUR OF CLINOCHLORES OF DIFFERENT POLYTYPES (KORSHUNOVSK ORE DEPOSIT)

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Among the rock-forming chlorites of the Korshunovsk ore deposit the unique gem one with jewelry properties is displayed. Both chlorite varieties have the similar chemical compositions represented by Mg-rich clinochlore with a very low Fe/(Fe+Mg) ratio. Their Al^{IV} and Al^{VI} contents range from 0.89 to 1.26 f.u. and from 0.86 to 1.14 f.u., respectively.

In comparable study of structural features of these chlorites by X-ray powder diffraction and IR-spectroscopy it has been established that rock-forming chlorite is represented by the most abundant polytype *IIb* with monoclinic cell (β = 97°), whereas among gem material along with *IIb* chlorite there is chlorite formed by packets of *Ib* polytype with orthorhombic unit cell (β = 90°). Both these polytypes are essentially distinguished by their thermal behaviour.

The investigated *IIb* chlorites have the DTA curves typical for powdered Mg-chlorites such as pennine and clinochlore. The DTA curves of these two chlorites exhibit two distinct endothermic peaks: the first more intense one at 600 °C is due to dehydroxylation from the interlayer octahedral sheet (brucite-like sheet) and the second peak around 800 °C is due to dehydroxylation from the 2:1 layer (talc-like layer), the latter peak is immediately followed by the exothermic peak at 860 °C corresponding to the formation of spinel and olivine. It is shown from TG curve that the water content corresponding to the first endothermic peak ranges from 7.7 to 8.3 % and that corresponding to the second peak ranges from 2.8 to 3.5 %. The total water content is 11.7-12.3 %.

The DTA curve of *Ib* chlorite also exhibit two distinct endothermic peaks, but the first peak at 690 °C is displayed less intense than the second one at 800 °C. The exothermic peak is unavailable on the DTA curve of *Ib* chlorite up to 1000 °C. The curve shows that the water content corresponding to the second peak is as much as 7.7 %. The total water content is about 10 %.

In all, the DTA and TG curves of *Ib* chlorite are characteristic for those of the mixture of Mg-chlorite with serpentine-like mineral. The serpentine-like properties of *Ib* chlorite are manifested in its X-ray diffraction pattern (very weak and diffuse 14 Å basal reflection) and in its IR-spectrum, which is practically similar to that of Al-serpentine of the analogous composition. The higher temperature of the dehydroxylation from interlayer octahedral sheet and "rearrangement" of the hydroxyl groups between the interlayer octahedral sheet and 2:1 layer bear witness to more strongly bounded hydroxyl groups in *Ib* chlorite as compared with *IIb* one. The essential differences between the properties of chlorites of *IIb* polytype ($\beta = 97°$) and *Ib* polytype ($\beta = 90°$) are specified considerably by weaker interlayer hydrogen bonds in the *Ib* chlorite structure.

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THE ROLE OF CLAYS AND HUMIC ACIDS IN MIGRATION PROCESSES OF ACTINIDES AND LANTHANIDES IN THE ENVIRONMENT

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The distribution of various toxic contaminants in the environment is determined, in the first place, by their interaction with highly dispersed constituents of soils, bottom sediments of rivers and lakes etc. The most typical representatives of these constituents are clay minerals.

Lanthanides and actinides are among the most dangerous inorganic toxins. A great amount of them were spread in the environment after the Chernobyl accident. Their typical feature is an ability for to combine with the surface active groups of clays and also with various groups of natural organic molecules. But now it can be concluded that a lack of experimental data and understanding exists on the influence of natural humic and fulvic acids on the sorption processes.

The objective is to study the interaction of lanthanides and actinides with the most typical representatives of various structural classes of clay minerals (kaolinites, montmorillonites, illites) in the presence of humic substances in order to determine how to improve the isolation of radioactive wastes with the usage of clay barriers.

Data have been obtained showing that the influence of dissolved organic matter on the sorption processes of actinides and lanthanides on clays may be manifold. Depending on the pH of the medium and concentration of humic substances there can be either stabilization of metals in the solution due to the formation of unadsorbed complexes, or an increase in adsorption, when the present molecules act as bridges between the surface and the ions. The structure of the possible surface complexes are proposed.

Practical recommendation are given for the usage of modified clays in clay barriers to exclude lanthanide-organic and actinide-organic complexes from ground waters.

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APPLICATION OF METHYLENE BLUE TITRATION FOR DETERMINATION OF CATION EXCHANGE CAPACITY IN DIFFERENT TYPES OF CLAYS

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In this paper a comparative study of results obtained for CEC determination according to ammonium-acetate method and by titration with methylene blue is presented. The main characteristics and advantages of each method are analyzed. The mineralogical content of each investigated clay was determined by: X-ray, IR, TGA and DTA analysis, as well as by chemical and rational analysis.

For each of the applied methods the obtained results were statistically tested by the determination of standard deviation and differences of values in parallel probes. It is shown that these statistical values are strongly depended on the type of clay, that is the present clay minerals in them. According to statistical values methylene blue titration seems to be more reproducible method.

The relation of experimental values obtained by methylene blue titration ($CEC_{m.b.}$) and by ammonium-acetate method ($CEC_{am.ac.}$) also depended on the type of clays as it can be seen from the review:

TYPE OF CLAY	CECm.b / CECam.ac
Kaolinite	1.00
Kaolinite-illite	1.86
Illite-kaolinite	0.52
Illite	0.62
Montmorillonite-illite	0.81
Montmorillonite	0.64

For illite and montmorillonite types of clays better values for the relation of CEC values determined by both methods (0.99 and 1.07) is obtained only in the case of the titration of homoionic forms (Ca and Na) of these clays by methylene blue.

The presented analysis of the obtained results according to both methods clearly shows that the method for CEC determination by methylene blue titration can be successfully applied only to kaolinite type of clays in heteroionic form. For illite and montmorillonite clays this method can be applied only to homoionic forms of clay. In that case all the advantages such as: short time of determination, simple equipment, less experiance, etc. of the methylene blue titration method disappeared.

ACIDITY OF MONTMORILLONITE PILLARED BY ALUMINA, ZIRCONIA AND CHROMIA

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Acidic properties of Al-, Zr- and Cr-pillared monmorillonites prepared from Jelšový Potok bentonite (Central Slovakia) were investigated using temperature-programmed desorption of ammonia. The number of acid sites varied with different interlayer cations from 0.06 to 0.23 $\mathrm{mmol.g^{-1}}$. The character of acid sites was similar in the case of Al- and Zr-forms. It is obvious that the chromium analogue contains less acid sites, nevertheless these seems to be stronger compared with Al- and Zr- pillared montmorillonites.

WEATHERING OF BENTONITE FROM STARÁ KREMNIČKA - JELŠOVÝ POTOK (CENTRAL SLOVAK NEOVOLCANITES)

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The existence of hypergenic kaolinization of bentonite in the 2 m deep vertical profile has been studied in presented paper. Primary montmorillonite was formed in the fresh water environment by alteration of rhyolitic tuffs in the diagenetic stage.

The published results are based on data obtained by XRD, IR spectroscopy, surface area measurements and total organic carbon analysis. Special attention is dedicated to an experimental verification of the possible origin of kaolinite during pedogenetic weathering of bentonite in the presence of humic acids.

Used methods confirmed that by the weathering caused degradation (dissolution) of bentonite and kaolinite formation at the same time. During the weathering release of Si, Al, Mg, Ca and Na from the bentonite was observed.

HUMIDITY SENSITIVE MINERALS

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Some minerals change when exposed to atmospheres beyond the range of relative humidity adequate to their stability field. Highly hydrated minerals (e.g. trona $Na_2CO_3.10H_2O$ and ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$) with high number of water molecules dehydrate in time when exposed to dryer atmosphere; they loose stepwise molecules of crystal water. The dehydration is related to either structural rearrangement towards the anhydrous form or to the total decay.

Similarly, anhydrous minerals (e.g. portlandite CaO and allite Ca_3SiO_5) or minerals partially hydrated (e.g. bassanite $CaSO_4.½H_2O$) rehydrate in minerals with higher crystal water content and with different structures. Some hydration/dehydration reactions are fully or partially reversible, sometimes with an extended hysteresis. Reaction rates can be also different.

Some clay minerals are also humidity sensitive. Their structure changes in atmospheres of different relative humidity due to water uptake or removal and also due to a re-arrangement of water molecules in inter-lamellar spacings. Subsequently, expansion or shrinkage results and it can be measured by changes of d_{001} spacing. Most sensitive to humidity changes are smectites. The water uptake is controlled by layer charges and by hydration energies of present exchangeable cations. If the cementing amorphous phases are present they might have an important role by hindering or avoiding swelling and shrinkage. Hydration of smectites saturated with cations with high hydration energy can lead to the liquefaction of clay powder into a suspension.

Hydration of smectite crystallites proceeds irregularly in bodies of aggregates and crystallite stacks so that a deformation of clay mineral crystallites is obvious. Deformation of clay mineral crystallites is pronounced by line broadening and shifting of the basal reflection line (001).

Beside smectites, several other clay minerals (e.g. illite and palygorskite) are humidity sensitive. Some illites show for instance a slight expansion at 0 % relative humidity. Also amorphous clay minerals and quasi-amorphous precursors of clay minerals (precipitates and hydrolysates) generated by grinding in water are humidity sensitive and formation of neoformed clay minerals can be observed. Reaction rates of structural changes can be estimated and phase transformations can be reconstructed.

Humidity sensitive minerals are studied by means of humidity controlled X-ray powder diffraction (Kühnel & Van der Gaast 1993). Changes in minerals are examined in situ (in one preparation which is placed and conditioned in wetted helium) in the specimen chamber of the diffractometer. Data on d_{001} values of Me^+ and Me^{2+} saturated montmorillonites from Upton, Wyoming, USA are included in the following table.

Table: Spacing, intensity and line broadening of basal reflection (001) of homoionic monmorillonite (Upton, Wyoming, USA) at different relative humidities.

	Li-saturated			Na-saturated			K-saturated			Rb-saturated			Cs-saturated		
R.H.	d(A)	Int.	FWHM	d(A)	Int.	FWHM	d(A)	Int.	FWHM	d(A)	Int.	FWHM	d(A)	Int.	FWHM
100	18.66b	13	5.4	18.66b	6	5.4	19.00	17	7.95	19.51b*	3.3	2.95	12.49	18	1.1
90	15.84	78	1.35	15.64	148	1.0	14.92*	28	3.2	15.14*	3.0	3.2	12.49	36	0.95
80	15.79	76	1.4	15.50	141	0.9	12.69*	42	3.1	15.09*	3.0	3.2	12.52	39	1.0
50	12.72a	79	2.0	12.70a	131	1.15	12.27a	56	2.0	12.52a	4.1	2.5	12.63	55	0.85
20	12.49	53	0.95	12.41	134	0.8	11.60	47	1.75	12.02	3.9	1.7	12.38	49	0.85
10	12.27	44	1.05	11.39	60	1.3	10.86	40	1.70	11.52	3.7	1.4	11.95	33	1.15
0	11.68	36	1.3	10.04	56	1.0	10.62	52	1.35	11.05	4.2	1.5	11.26	52	0.9
	Mg-saturated			**Ca-saturated**			**Sr-saturated**			**Ba-saturated**			**Explanations/units**		
R.H.	d(A)	Int.	FWHM	d(A)	Int.	FWHM	d(A)	Int.	FWHM	d(A)	Int.	FWHM	d — spacing (Å) Int. — intensity (c/s) FWHM — full width half maximum (°2θ), b — diffuse line, * — double line a — strongly asymmetric line		
100	19.29	188	0.7	19.29	132	0.70	19.54	94	0.65	19.40	60	0.63			
90	16.04	256	0.7	19.79	202	0.65	16.14	150	0.60	16.39	99	0.60			
80	16.04	281	0.7	15.69	207	0.65	16.14	157	0.60	16.34	101	0.60			
50	15.34	306	0.7	15.39	233	0.60	15.69	156	0.55	12.90	48	1.20			
20	14.32	222	0.85	14.50	104	1.35	12.71	114	0.65	12.63	94	0.55			
10	13.91	193	1.0	12.69	89	1.40	12.47	135	0.65	12.50	95	0.6			
0	11.93	165	0.95	11.83	100	1.10	11.45	72	1.15	11.67	51	1.10			

CLAY MINERALS – HUMIC ACID SYSTEMS: Cu(II) SORPTION STUDIED BY MEANS OF MODIFIED ELECTRODES

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Carbon paste electrodes (CPEs) modified with clay minerals are successfully used in voltammetric analyses (Kalcher 1990; Kula & Navrátilová 1996) as well as in study of sorption processes on the clay minerals (Fitch 1990; Kalcher et al. 1995). The influences of humic acids present in the solution on the Cu(II) sorption on the clay was found by means of voltammetry on the clay modified CPE (Kula & Navrátilová 1995), montmorillonite-humic acid system was also studied (Chassin et al. 1978).

Montmorillonite-humates, vermiculite-humates and kaolinite -humates with various content of humic acid were prepared. Their basic structural properties were studied by means of X-ray diffraction and IR spectrometry.

Carbon paste electrodes modified with humates MMT-HA, VER-HA and KA-HA were used for voltammetric study of Cu(II) sorption. Humic acid bound onto the clay mineral surface changed its ion-exchange properties.

Two types of clay-humates were prepared. It was found, that binding of humic acid on the clay depends on the method of preparation. Both types of clay-humates exhibited decreased sorption of Cu(II) in comparison with clay minerals alone. The comparison of pH dependences of sorption for various type clay-humate implicates, that HA molecular arrangement in clay-humates particles is probably different. It seems, that it is similar to the clay-humate structure described by Chassin (1978).

Voltammetric measurements on the CPEs modified with two types of clay-humates and with their components alone implicates:

— both types of clay-humates can be distinguished, it is possible to deduce the probable arrangement of HA molecules on the surface of the MMT particles,

— possibility of utilization of voltammetry with modified carbon paste electrodes for study of soil system components.

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FRACTURE FILLING ENDELLITE FROM IITTALA, FINLAND

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The first endellite (10 Å -halloysite) reported from Finland has been met with in Iittala, southern Finland. The host rock consists of schistose mafic volcanites: agglomerates and uralite porphyries. The weakly schistose volcanite turns slowly into a zone of strongly schistose, breccia like rock with

1-2 cm wide, randomly directed fractures filled with white, yellowish or reddish endellite. The width of this zone is several metres.

The mineral was identified using XRD, IR and DTA-TG techniques. The IR-method seems to give a means of distinguishing dehydrated endellite (7 Å variety) from kaolinite. The average chemical composition determined with the microprobe is 33.59 % SiO_2, 40.09 % Al_2O_3, 0.03 % TiO_2, 0.01 % Fe_2O_3 (tot), 0.03 % MgO, 0.74 % CaO, 0.06 % Na_2O, 0.02 % K_2O, 0.16 % F_2, 1.27 % Cl_2 and 24.08 % H_2O. The CaO and Cl_2 contents are markedly high, however, no extra phase has been encountered. Clay minerals are hardly, if ever, pure but usually contain impurities. The only impurity found in the Iittala endellite is iron pigment, or occasionally a small amount of contaminating amphibole from the host rock.

The endellite occurs either as a soft paste varying in colour from white to reddish brown or as a very dense white or slightly coloured substance resembling dryed gel. Sometimes uncoloured transparent spheres, less than 0.5 mm in diameter, appear in the outer parts of the latter type. Furthermore, much smaller spheres occurring in clusters make up a coral like structure. Scanning electron microphotography showed that the mineral has a platy morphology instead of the typical tubular one.

Usually acidic rocks generate kaolinite minerals and Ca- and Na-rich rocks montmorillonite during weathering processes. Kaolinite may also be derived from impure limestones or porphyritic volcanites. Halloysite has been reported to form by the action of sulphate-bearing solutions on kaolinite leading to gel formation and subsequent recrystallization. This is thought to apply also for the Iittala endellite.

Fe-MINERAL IDENTIFICATION IN THE SMOLNÍK ACID MINE WATER OCHRE PRECIPITATES

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A short time after the definitive ending of exploitation of the cooper-pyrite ore deposits at Smolník and floading of the mine workings, there was a very large increase in the acidity of the water in the Smolník Stream. The Smolník Stream water has been contaminated by drainage of water from the mine, and in the most polluted part of stream (near the mine workings Pech and Karitas) the water pH values have been in the range 4.5 to 2.3. The atmosferic oxidation of sulfides, mainly pyrite, and subsequent release of H_2SO_4 and Fe to leaching water are well-known processes of mine water acidification. A large amount of Fe-ochre precipitates have been formed along both sides of the stream and also in the stream sediments. We have studied fresh precipitate samples and also samples of the ochre hardpan by X-ray diffraction, SEM, IR and TEM methods. The Fe, Al, Si and S contents in the mineral grains have been obtained with LINK-analysator in TEM study.

We have found, that most of the ochre samples have been formed by poorly crystallized extremely fine grained Fe^{3+} mineral. Scanning electron micrographs showed spherical, about 1 μm large, particles with spicules. The spicule crystals are only 10 to 30 nm large and in TEM micrographs they appeared as aggregates of rod-like particle and also aggregates with unique pin-cushion morphology. LINK-analyses showed that these rod-like and sheet crystals contain only Fe, but aggregates with pin-cushion morphology contain also S (values of grain Fe/S ratio are between 6-9). The presence of SO_4^{2-} has also been confirmed by IR analyses of samples. Because, X-ray records allowed the clear identification mineral jarosite only in trace content, we have suggested, that the samples contain a relatively large amount of the second sulfate mineral, Fe^{3+} oxyhydroxy sulfate — schwertmanite. Jarosite and schwertmanite have formed in the very acid area, just after mine drainage water mixes with stream water. At this time, the pH values of water increased only slightly (2.9-3.6) because the mine waters carried a relatively high content of dissolved solids (TDS about 30-40 g/l). The mineral goethit has been formed in large content relatively later, after acidity and SO_4^{2-} have been decreased by mixing with fresh (atmospheric) water and CO_2. Halloysite probable also formed in the acid area and has been observed as alongated, 1-4 μm large crystals, with characteristic roled up in tube morphology, composed only of Al and Si (oxygen) elements. The mine drainage water has a high concentration of dissolved Al (more than 1000 mg/l) and also hydrated silica, and it is the result of sulfuric acid dissolution of rock alumosilicate minerals.

INTERCALATION OF [Ni(4-ETHYLPYRIDINE)$_4$NCS)$_2$] COMPLEX IN MONTMORILLONITE

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Montmorillonite and its Zr-pillared analogue were used as the host components to interact with ethanol solution of [Ni(4-Etpy)$_4$NCS)$_2$] complex. Ni(II) complex has a monomeric molecular structure in the solid state and Ni atom occurs in a distored compressed pseudooctahedral configuration formed by two atoms from the NCS groups and four atoms from the 4-ethylpyridine ligands with a propeller conformation. The complexes of this type are used as the host phases for preparation of Werner clathrates.

Ca-montmorillonite and Zr-pillared montmorillonite were prepared from the < 2 μm fraction of bentonite Jelšový Potok (Central Slovakia). The results revealed that Ca-monmorillonite as well as Zr-PILC have provide a suitable reaction media for the incorporation a neutral complex [Ni(4-Etpy)$_4$NCS)$_2$] into the interlayer space. Using XRD and IR spectroscopy it was found that Ni complex enters in the porous system, but in interlayer space Ni complex has a different arrangement of the NCS groups after interaction with the host structure.

Thermal analysis of intercalation products revealed the stepwise release of four ethylpyridine ligands in the sequence 2 : 1 : 1 and the oxidative decomposition of NCS groups. These facts leads to the assumption a new properites of Ni complex fixed into the porous silicate systems could be generated.

MINERALOGICAL AND CHEMICAL INVESTIGATION OF DIOCTAHEDRAL CLAYS BY FTIR SPECTROSCOPY

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Mineralogical and chemical composition of twelve smectites and nine illites of various geological origin were examined by FTIR spectroscopy. Some of the < 2 μm fractions were pure, but in others admixtures such as kaolinite, cristobalite, quartz, amorphous SiO_2, carbonates or boehmite were identified. The FTIR spectra confirmed that Al-rich montmorillonites were formed by diagenetic alteration of rhyolite tuffs (Jelšový Potok) or by hydrothermal alteration of rhyolites (Stará Kremnička). Both the position of the OH stretching band near 3620 cm^{-1} and the shape of the pattern in the OH bending region reflected partial substitution of octahedral Al with Mg, and low Fe content in these smectites. Fe-rich montmorillonites (Hrochoť, Zvolenská Slatina) or nontronites (Sampor, Badín) are products of weathering of andesites and their tuffs or of basalts (Jelšovec). Both the AlFeOH band near 880 cm^{-1} and the FeFeOH absorption near 820 cm^{-1}, which is characteristic for nontronites, indicated higher Fe content in these samples.

The absorption bands near 828 and 754 cm^{-1} revealed illite layers in rectorite Červená Studňa and in other samples containing illite (Šobov, Hodruša). The IR spectra of mixed-layer illite/smectite minerals (Dolná Ves) reflected various amounts of expandable layers. The intensity of the band at 424 cm^{-1}, which is present in the spectra of illites, but not in those of smectites, significantly increased with decreasing expandability; i.e. with the increasing illite content. On the other hand, the absorption near 620 cm^{-1}, characteristic for Al-rich montmorillonites, decreased in intensity with the decreasing smectite content.

CLAY MINERALOGICAL INVESTIGATIONS OF TERTIARY CLAY FROM NORTHERN BOHEMIA

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The great mining activity in northern Bohemia results in large pits which are backfilled with Tertiary clay. Vanicek & Kazda (1995) investigated the transport of pollutants in the consolidated backfilled clay by two dimensional finite element calculations. The estimated parameters used in the calculation were: advective transport, diffusion, and mechanical dispersion. Adsorption on clay minerals was not taken into account.

The mineralogy of two tertiary clay samples from the Jan Šverma-Holisice and CSA mines was investigated. The goal of the investigation was to obtain better parameters for further finite element calculation and to get a first estimation of the adsorption capacity of the material.

Composition of the bulk material: clay minerals, quartz, feldspars, calcite

Sample	Carbonate content %	Fraction < 2 μm %	External surface m^2/g	Adsorbed water at 75 % rel. humidity	Total surface area m^2/g	Cation exchange capacity meq/100g
J. Sverma	4.5	77	48	6.79	200	29
CSA	3.0	71	43	5.38	160	24

Exchangeable cations:

Sample	Ca meq/100g	Mg meq/100g	Na meq/100g	K meq/100g
J. Sverma	12.40	12.28	0.77	0.95
CSA	7.78	11.29	1.06	0.64

Sample	Fe meq/100g	Mn meq/100g	Cu meq/100g	Zn meq/100g
J. Sverma	0.009	0.39	0.024	0.034
CSA	<0.001	0.031	0.024	0.004

Composition of the clay fraction:

Sample	Smectite %	Kaolinite %	Illite %	Quartz %
J. Sverma	40	15	40	5
CSA	35	20	35	10

Because of the high clay mineral content, the high cation exchange capacity and the large surface area of the clay is well qualified as barrier material for waste. Further investigations are planned to determine diffusion coefficients, hydraulic conductivity, and adsorption capacity for various chemicals.

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CONTRIBUTIONS TO THE CLAY MINERALIZATION AND ZEOLITIZATION OF MIOCENE TUFFS IN THE MECSEK MTS., HUNGARY

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Stratigraphically two types of tuff, tuffite and tuffaceous horizons of Miocene age occur in the Mecsek Mountains of Hungary. The lower one is rhyolite tuff (19.0 ± 1.4 Ma), the "middle" one is dacite tuff (16.4 ± 0.8 Ma). The rhyolite tuff consists of ash-flow and ash-fall tuffs, while the dacite consists of ash-fall tuff only.

Most of these horizons are partly or completely altered. The alteration products are smectite, cristobalite, clinoptilolite, kaolinite, chlorite, illite, illite/smectite mixed layer mineral, and in trace amount mordenite, calcite, dolomite, geothite, kaolinite/smectite mixed layer mineral.

Different scale of zeolitization or no zeolitization can be observed the tuffs and tuffites. The zeolitization of the rhyolite ash-flow tuff is extensive, it is sporadic in the dacite ash-fall tuff, and there is no zeolitization in the rhyolite ash-fall tuff (Polgári et al. 1995). The zeolite mineral is clinoptilolite/heulandite. Mordenite occurs in trace amount beside clinoptilolite only in one borehole penetrating the rhyolite ash-flow tuff.

The chemical composition of the zeolite mineral varies around the 1 : 1 ratio of (Ca+Ba) : (Na+K), which is the border between the clinoptilolite and heulandite definition according to the nomenclature of Mason & Sand (1960).

Smectite is ubiquitous, it can be found in the highly zeolitized rhyolite ash-flow tuff as well as in the non zeolitized, but altered dacite tuff. The *d* value of the basal reflection of smectite varies from 11.6 Å up to 17.0 Å. It is well known that this *d* value determined by the type of interlayer cations and the amount of water molecules between the TOT sheets. The *d* value is higher (14–17 Å) when the interlayer dominant cation is Ca, and it is lower (11–14 Å) when the interlayer dominant cation is Na or Fe.

There is a relation between the *d* value of the smectite basal reflection and the zeolitization. When the rock is zeolitized, the smectite *d* value ranges between 11.6 and 14 Å. When there is no zeolite mineral together with smectite, the latter's *d* value varies between 14 and 17 Å. The reason for this phenomenon is the distribution of Ca^{++}, Na^{+} and K^{+} between clinoptilolite and smectite. The formation of smectite and zeolite phases were affected by the cooling rate (Yamada et al. 1995), as well as by the geochemical environment, Eh and pH conditions.

A detailed description and explanation of this phenomenon will be given.

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EQUILIBRIA OF THE EXCHANGE REACTION BETWEEN CALCIUM AND COPPER ON MONTMORILLONITE IN DEPENDENCE ON TEMPERATURE

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Reactions of the cation exchange which include metal traces of transitional elements are significant from the environmental pollution viewpoint and the role of copper and zinc as microelements in plants metabolism and recultivation of barren soil. Copper is essential for many of the life processes of the plant, notably in enzymatic and catalytic reactions. The specific role of Cu is a still unsolved scientific problem.

There are, however, very few data in literature concerning the influence of temperature on cation exchange equilibrium, especially for transitional elements. The aim of this paper is to study the mechanism of the ion exchange of calcium by copper on Ca-montmorillonite in dependence on temperature.

This work examined the equilibria of calcium exchange reaction by copper on Ca-montmorillonite at three temperature levels: 20 °C, 40 °C and 60 °C in the mixture of solutions 0.1 M $CaCl_2$ and 0.1 M $CuCl_2$ for four different mole ratios (4 : 1, 3 : 2, 2 : 3 and 1 : 4) and 2 g of montmorillonite.

At each temperature equilibria isotherms, selectivity coefficients and the standard free energy of reactions were defined. From the temperature dependence of the selectivity coefficient and standard enthalpies of exchange reactions were calculated for the researched temperature interval. The starting experimental material was montmorillonite Wyoming, particles fraction below 3 μm. The exchange capacity (CEC), determined by the ammonium-acetate method, had the value 78 mmoles M^{+}/100 g. The exchangeable cations Ca, Mg, Na and K were determined by atomic absorption and flame photometry. The homoionic form of Ca-montmorillonite was obtained by exchange reaction, multiple processing of Wyoming by 0.5 M $CaCl_2$ solution. The exchange reactions were carried out by the shaking-standard laboratory method.

The equilibrium of reaction Ca-Cu exchange at 20 °C is favorable in relation to copper. A temperature increasing from 20 °C to 40 °C is favorable in relation to further copper adsorption. The equilibrium isotherm at 60 °C is exceptionally favorable in relation to copper. Selectivity coefficients of Ca-Cu exchange at 20 °C, 40 °C and 60 °C depend on saturation by copper. Selectivity coefficient of Ca-Cu exchange at 60 °C has the highest value. The standard free energy of Ca-Cu exchange reaction is different for different degrees of saturation by copper and has negative values during the complete course of exchange reaction for all the three studied temperatures.

The values of selectivity coefficient, obtained by experiment, in tested systems depending on temperature

$$K^{Cu}_{Ca\ 60\,°C} > K^{Cu}_{Ca\ 40\,°C} > K^{Cu}_{Ca\ 20\,°C}$$

show that the increasing of temperature has a positive effect on the exchange reaction.

The dependence of $\ln K^{Cu}_{Ca}$ of saturation degree of Cu^{2+} ion indicates an irreguler behaviour of the Ca-Cu system exchange reactions and the presence of heterogenic places for the exchange and confirms montmorillonite as a polyfunctional cation exchanger.

THE CLAY MINERALS OF WEATHERING CRUSTS IN ASIAN PLATOBASALTS AND THE EVOLUTION OF THE CENOZOIC CLIMATE

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Platobasalts are world-wide geological objects. The weathering of basalts bears a memory of climatic conditions at the time of weathering. After its formation the weathering crust (WC) is preserved by the under- and overlaying basalt layers.

The weathering crust minerals (WCM) are good climate indicators: montmorillonite (MM) is formed in the semiarid conditions, kaolinite (KL) and halloysite (HL) — in the warm humid conditions, KL and gibbsite (GB) — in the hot humid climatic conditions.

Information about the age of basalt layers (K-Ar dating) and the corresponding CM types allows us to reconstruct paleoclimates.

The samples were taken from platobasalts of the Russian Far East (6 age levels), Vietnam (2 age levels) and Syria (3 age levels). The results of the climate restoration for the Russian Far East during the last 50 Ma are shown in the table:

CW mineral types and evolution of the Russian Far East Cenozoic climate.

Region	Age of basalts, eclosing CW	Age of CW (Ma)	Mineral type of CW	Climate
The Central Sikhote-Alin	4.5 ± 0.4	Pliocene (Q1<CW1<4.5)	MM	Semiarid
- " -	4.5 ± 0.4 7.7 ± 0.7	Late Miocene-Early Pliocene (4.5<CW2<7.7)	HL	Warm humid
- " -	15.4 ± 0.5 16.3 ± 0.4	Middle Miocene (15.4<CW3<16.3)	MM	Semiarid
The Southern Sikhote-Alin	21.2 ± 0.5 22.0 ± 0.4	Early Miocene - (21.2-no CW-22.0)	None	Cold arid (?)
The Northern Sikhote-Alin	31.4 ± 1.6 36.9 ± 1.6	Early Oligocene (31.4<CW4<36.9)	MM	Semiarid
- " -	39.0 ± 1.0 41.5 ± 1.1	Late Eocene (39.0<CW5<41.5)	MM	Semiarid
The Southern Sikhote-Alin	51.4 ± 2.0	Early-Middle P2 (Pg<CW6<51.4)	KL, GB	Hot humid

The paleoclimatic reconstruction based on the WC clay minerals study is in good agreement with biogenic and isotopic data.

HYDROLYTIC REACTION OF WATER WITH ALUMINUM CATALYZED BY CLAY MINERALS

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Aluminum oxide coating protects aluminum metal from spontaneous reaction with water. It has long been known that acids will dissolve this coating and the metal beneath it. But it has not been recognized that clay minerals, in contact with aluminum in a suspension having an overall neutral pH, also may attack this coating leading to the formation of gaseous and solid reaction products and an electrical potential. The application of a dilute clay suspension (1 mg clay per ml distilled water) to an aluminum plate, after an incubation period of several hours, results in the formation of hydrogen gas, aluminum hydroxide compounds such as bayerite, nordstrandite, and diaspore, and corrosion pits in the aluminum surface. Hydrogen gas was determined by gas chromatography, and preliminary measurements yield a potential of 1.3 V between the suspension and aluminum plate. The reaction continues for as long as the suspension stays in contact with the aluminum surface, but the reaction does not occur with a thick clay coating (smear slide). Water alone produces no observable reaction with the metal. The reaction is not affected by the type of aluminum alloy used, and is promoted by different kinds of clay, including smectite, mixed-layer illite/smectite, and even kaolinite.

A reaction catalyzed by clay minerals is proposed, in which clay minerals in contact with the surface permit proton penetration of the protective aluminum oxide layer. Clay minerals prevent self-healing of the aluminum oxide layer, and promote the hydrolytic reaction of water with aluminum:

$$2Al + 6H_2O \xrightarrow{clay} 3H_2 + 2Al(OH)_3$$

The clay serves as a semi-permeable membrane, provided that the clay layer is not too thick, thereby allowing water to diffuse to the clay-metal interface, where hydrolysis takes place.

Speculations concerning practical implications of the reaction are as follows. The phenomenon could be used for local energy production either by burning the hydrogen gas, or by using the electric current. Enhanced corrosion of economically important aluminum by clay dust is a long-term problem. The risk of hazardous fire and explosion caused by hydrogen gas production in waste sites where aluminum metal and clay particles interact also could occur. On the other hand, clay catalyzed corrosion of aluminum could release electrons to decompose toxic organic compounds.

INTERSTRATIFIED KAOLINITE/ SMECTITE MINERALS IN AUSTRIA

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In contrast to the common illite/smectite and chlorite/smectite mixed layer minerals, only very little information can be found about kaolinite/smectite mixed layers in the scientific literature. Nevertheless, this mineral was first described 40 years ago. In Europe this type of mineral was previously only known to occur in Great Britain, Spain and Poland. It was also synthesized in Poland by Środoń 1980.

In Austria the first kaolinite/smectite mixed layer was detected in samples collected during mass-movement studies in the Hausruck area (Upper Austria). The geologic strata belong to the Austrian Molassezone where tertiary clays and coal layers have been sedimented together. Coal was mined in this area in former times. One sample was taken from the lower bed and another sample from an interlayer in a coal horizon.

The mineralogical composition of the bulk samples and several fine fractions (20, 2 and 0.2 μm) was determined by XRD. Identification of the mixed layer mineral was achieved with oriented samples after saturation with Mg^{++} and K^+, solvation with ethylenglycol and DMSO, and contraction after heat treatment (300°, 550 °C). The quantitative estimation of kaolinite and smectite in the mixed layer mineral was performed according to Moore & Reynolds Jr. (1989). The program NEWMOD was used to confirm these results.

The bulk samples from both locations have a high quartz content. The 2 μm fraction consists mainly of smectite, the mixed layer mineral and small amounts of illite. The mixed layer mineral is randomly interstratified (R0). The proportion of kaolinite and smectite in these samples depends on the grain size. For both samples the kaolinite content of the mixed layer decreases with grain size. The 2 μm fraction contains about 80-90 % of the kaolinitic component, while only 50 % is present in the 0.2 μm fraction.

The results of this investigation provide information about the development of kaolinite/smectite mixed layer minerals.

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CONTROL OF INTERFACE AND INTERPARTICLE CLAY REACTIONS

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One of the main goals of ceramic processing is to achieve a high density and strength of the solid body based on clay slurries. In our earlier works the regularities of the rheology property changes of consolidated green-bodies were studied. It was shown that the main role during manipulation of the powder-like state of clay suspensions belongs to the reactivity of their surface, i.e. the acid-base balance at their interface. Numerous papers are devoted to search for the additives able to lubricate effective rearrangement of particles and thus to produce other low viscosity slurries through manipulation of short-range forces.

We tried to develop the idea of surface active sites (SAS) direct or indirect participation in interparticle bond formation during the green-body transformation to the ceramic one. The rheology of powder-like and other consolidated states depend on the rheology (SAS parameters) of clay suspensions or slurries.

The aim of the present work is to find a rational method for controlling clay surface reactions during their treatment. Natural and modified kaolinite samples as well as powders of dispersed glasses served as objects of the investigation.

The number of acidic centers of Brönsted (B) and Lewis (L) types, and the specific surface electroconductivity upon heating the samples were measured. The values of total sample strength, the strength and number of individual contacts were estimated on the basis of experimental techniques and model presentation.

According to our opinion, the individual contacts between the clay or glass particles form for account of acid-base interactions and hydrogen bonds formation between the Brönsted sites. During heating there are significant interface transformations taking place causing B-sites to change into L-sites and changes in all the physico-chemical and physico-mechanical parameters of consolidated bodies. The presense of high acidic L-sites and the probability of occurrence of thermofluctuation processes leads to transformation of donor-acceptor bonds to the strong chemical Si-O-Si, Si-O-Al etc. bonds.

The reactivity of the systems was changed with the help of different modifiers: inorganic salts, organic compounds of siliconates series. In our experiments the reactivity was increased by the greatest degree by the sodium ethylsiliconate which results in the maximum values of the space structures in the dispersions.

Therefore, the consecutive inactivation of particle surface sites, the decrease in gaps between them and thermoactivation of donor-acceptor interactions are among the possible ways of the purposeful regulation of properties of ceramic bodies based on dispersed silicates.

HEATS OF IMMERSION IN METHYLENE BLUE SOLUTION AND ION-EXCHANGE OF TRIBOCHEMICALLY ACTIVATED CLINOPTILOLITE

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Tribochemical activation is a widespread method for modifying the structure of solids and for forming active centres on fresh surfaces. The zeolite samples obtained during ball milling have been characterized by different methods such as X-ray diffractometry, scanning-electron microscopy, IR spectroscopy and simultaneous thermal analysis but not by calorimetry.

Our intention was to investigate the heats of immersion and ion-exchange of tribochemically activated samples of clinoptilolite.

Clinoptilolite tuff from the Beli Plast deposit, SE Bulgaria (0.1-0.2 mm size fraction), containing about 80 % clinoptilolite was used in this study. The samples were tribochemically activated in an agate planetary ball mill (Fritsch Pulverisette) for time periods of 1 and 3 h. The heats of immersion of fully hydrated zeolite samples in water and methylene blue (MB) solution and ion-exchange in 1 M CsCl solution of samples were measured by Kalve type calorimeter at room temperature. The X-ray diffractograms were taken by a Dron 2YM diffractometer.

Our calorimetric results are summarized in the following Table.

Activation [h]	Heats of immersion and ion-exchange of clinoptilolite samples [J/g] in		
	H_2O	MB	CsCl
0	-0.5	-2.1 (-1.6*)	-16.5 (-16.0*)
1	-1.7	-3.5 (-1.8*)	-21.8 (-20.1*)
3	-1.5	-2.6 (-1.1*)	-21.6 (-20.1*)

* with correction for heats of immersion in H_2O

The highest activation effect on the heats of immersion and ion-exchange is observed at 1st hour. This indicates an improved optimum for dispersion of the zeolite particles provided by crack formation on the surface and separation of small fragments.

NON-MARINE GREEN CLAYS — THE CASE OF THE RONA LIMESTONE (SALAJ DISTR., RUMANIA)

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Non-marine green clays were the subject of several studies, some of them by Porenga (1968). The assigned mineralogical nature was variable — between a "ferriferous illite" and a "glauconitic illite", but the high crystallochemical similitude is obvious. This makes the attempt characterize such minerals quite difficult.

The Rona Limestone (Upper Cretaceous?-Lower Eocene) is a lacustrine carbonate deposit, located in the NW part of the Transylvania Basin. In the basal part of the classical profile a siliceous nodules ("septaria") level is worth mentioning. The "septaria" are coated with an intense-green coloured clay, which constitutes the subject of this study.

The XRD on oriented samples indicates the presence of an opened (degraded) illite. The Mössbauer spectra show 4 doublets, for both ferric and ferrous cations, in both M1 (trans) and M2 (cis) octahedral sites. The total Fe^{2+}/Fe^{3+} ratio is somehow at the limit of the values indicated by several authors for the glauconitic minerals. Fe^{3+} preferentially occupies M2 sites and, especially, Fe^{2+} occupies M1 sites.

The first O and C isotopic measurements in Rumania were performed on ten samples from the Rona Limestone: nine on carbonate samples, and one on the green clay. An enrichment in ^{12}C is noticed, as a sign of the biogenic influences during the mineral formation. The corresponding values obtained for the green clay, plotted in the Milliman (1977) diagram indicate a fresh-water carbonate paleoenvironment.

The genetic mechanism of formation of the green clay must be very similar to the illitization process, through drying and wetting cycles, in weathering profiles. For the Rona Limestone, such relative sea-level changes may be assumed on the basis of sedimentological arguments.

PHYSICOCHEMICAL CONDITIONS OF SEDIMENTATIONS OF THE PERMIAN KUPFERSCHIEFER: VANADIUM AND COPPER

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Within the Central European Zechstein Basin the Permian Kupferschiefer has been deposited under anoxic conditions. In most parts of the basin, the metal content does not exceed values commonly observed in black shales. However, in areas near to the Zechstein sea-shore metal enrichment is observed. Organic geochemical analyses of this copper-mineralized sections in the Kupferschiefer from southwest Poland show that vanadyl (VO^{2+})-porphyrins (P) are common constituents of the shale.

Chemical conversion of V to VO^{2+} in the sedimentary water is strictly conditioned by the depositional environment. Both redox potential (Eh) and acidity (pH) are key factors in the preservation of VO^{2+} in this environment and their association with the organic materials. Thus, VO^{2+} is an excellent geochemical indicator of physicochemical conditions of sedimentation.

The stability field of VO^{2+} on the Eh-pH diagram, shown in Fig. 1, is constructed for seawater concentrations of: total V (3 ppb) and CO_3^{2-} (140 ppm). This field may be restricted by superimposing the Eh-pH field for P, Fig. 1. Thus, the aqueous environment should be in the region of 0.0 V to -0.2 V. Finally, the stability field of VO^{2+} in the presence of P is further restricted by the Eh-pH field for carbonate ions.

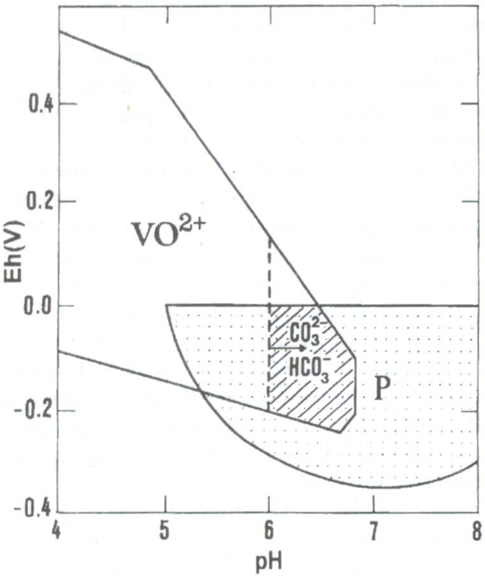

Fig 1. Eh-pH diagram showing approximate stability field for the P preservation (stippled area) and stability field for VO^{2+} (total [V] = 3 pbb) and carbonates ([CO] = 140 ppm) at 300 K and with p = 1 atm. Probable conditions in the sediment during the accumulation of the Kupferschiefer is represented by the shaded area.

From the chemistry of VO^{2+}, P and carbonates, it is deduced that the oxidation potential and pH of the interstitial seawater of the Permian (Kupferschiefer) sea was approximately 0.0 V to -0.2 V and 6 to 7, respectively, during the accumulation of Kupferschiefer.

VANADIUM IN THE MOONTEREY SHALE

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The vanadium was determined by emission spectrography in Monterey shale (CA) which is a sediment of the diatomic earth type. To obtain an indication of the chemical nature of vanadium (V) the samples were analysed at various stages of demineralization. It was found that for the samples containing less than 100 ppm of V around 59 % of V belongs to the mineral fraction soluble in cold 6 M HCl. For the vanadium-rich sample (above 100 ppm of V) the largest part of this metal belongs to the fraction soluble in warm 6 M HCl, probably in the form of hydrated oxides and vanadates. We also detected by electron spin resonance (ESR) vanadyl ion (VO^{2+}) associated with the clay fractions of the Monterey geological samples. Using the same technique we observed Fe^{3+} ion and Mn^{2+} ion in some of the Monterey shale samples.

RESEARCH ON STRUCTURAL CHANGES OF THE MONTMORILLONITE MINERAL WITHIN THE SYSTEM: MONTMORILLONITE, WATER, Na_2CO_3 AND $Mg(OH)_2CO_3$

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Alkali-magnesium activation of montmorillonite leads to significant changes in the rheological properties of the system compared to the characteristics of the initial system: montmorillonite-water. Explanation of the phenomenon of change in the rheological properties of the system: montmorillonite-water-electrolyte using the cation exchange method was not sufficient and required the multidisciplinary approach.

The system — montmorillonite extracted from "Jelenkovac" (Serbia) bentonite with fractions below 2 μm - water - Na_2CO_3 - $Mg(OH)_2CO_3$ was studied in detail.

Instrumental methods such as X-ray diffraction, infrared spectroscopy, differential thermal analysis and thermogravimetric analysis were used for tracking the structural changes.

The alternation of montmorillonite was observed by studying the structural changes in montmorillonite in the system: montmorillonite, water, Na_2CO_3 and $Mg(OH)_2CO_3$. A certain amount of aluminum is released from the octahedral layer during the process, enabling the creation of hydrotalcite in the presence of $Mg(OH)_2CO_3$ and Na_2CO_3. Hydrotalcite belongs to anionic clays and is created by isostructural exchange of Mg^{2+} ions in brucite by Al^{3+} ions, with positive charge of the octahedral layer of brucite as a consequence. Since the elementary particles of the montmorillonite mineral are negatively charged, montmorillonite and hydrotalcite become mutually attracted and aligned along the c-axis, which results in significant change in rheological properties, especially viscosity η (from 6 to 26 mPas).

The paper presents a contribution to study of the mechanism of changing the rheological properties of the system: montmorillonite-water-electrolyte, either through structural changes or through the interaction between the particles of cationic and anionic clay.

SORPTION OF CESIUM ON ALUMINOSILICATE

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Sorption of cesium on aluminosilicate was studied using cesium 137 radionuclide as a tracer. The main object of the study was illite, montmorillonite and zeolite of different type. The sorption parameters like sorption capacity for cesium, isotherm curve, influence of different cations used in electrolyte were determined using radioactivity measurement of 137-

cesium. The main advantage of such determination of cesium sorbed on inorganic materials was the possibility to find very selective site for cesium sorption. Those selective sites have very low capacity and can be determined only if a small fraction of sorption area is occupied by cesium. Langmuir or Freundlich sorption isotherms were used for calculation.

LIMNOGENIC ZEOLITES IN THE INDOCHINA MESOZOIC DEPOSITS

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Mesozoic deposits widespread in Indochina regionally show specific zeolite-bearing rock properties. This largely refers to volcanic-sedimentary complexes featuring (besides lake, littoral and shallow-water sediments of continental basins) a variety of acid and medium volcanics, ashes and other effusive material. These limnogenic complexes of rocks (mainly Jurassic-Cretaceous) are commonly associated with elongated paleodepression zones flanked by series of faults. Carbonate waters circulating through these faults interact with country rocks yielding zeolites. Zeolitization may also occur at the earlier sedimentation stages when the volcanic material gets directly into carbonate water basins.

By analogy with the studies zeolite-bearing regions, geological structures and stratigraphic intervals are identified in different areas of Indochina holding prospects for zeolites.

The types of genetic environments most favourable for zeolite-forming processes within the study region are considered. It is shown that the lithogenetic type of zeolitization includes the most promising subtypes of volcanic-limnic and marine diageneses. Such deposits have the highest industrial significance. To ensure the zeolite formation, the sediment must contain ash particles of acid or alkaline glass that would interact with poor-alkaline and alkaline water of paleolakes and continental paleoseas. The main zeolites are: clinoptilolite (formed in poor-alkaline environments), chabasite, erionite and phillipsite (formed in the soda lake environments).

CRYSTAL STRUCTURES OF TWO SYNTHETIC FERRUGINOUS CESIUM MICAS: CRYSTAL CHEMISTRY AND IMPLICATIONS FOR REFINEMENT TECHNIQUES

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Within a project aimed at synthesis and description of crystalline phases capable of binding radioactive ^{135}Cs and ^{137}Cs, we grew two ferruginous micas with Cs in the interlayer, namely Cs-annite and Cs-ferriannite, whose compositions correspond to formulas $CsFe_3^{2+}(AlSi_3)O_{10}(OH)_2$ and $Cs Fe_3^{2+}(Fe^{3+}Si_3)O_{10}(OH)_2$, respectively. Both were synthesized by standard hydrothermal techniques from an oxide mix, at 550 °C and 0.1 GPa water pressure.

Cs-annite grew as fine-grained aggregates, and the run products invariably contained some pollucite and magnetite (< 15 per cent). Cs-ferriannite grew as excellent crystals up to 1 mm across.

Using single-crystal intensities, the structure of 1M Cs-ferriannite was refined in the C2/m space group with R equal to 5.5 %. All octahedral positions as well as 23 % tetrahedral positions are occupied by iron. Its octahedral sheet is geometrically homooctahedral with all octahedra the same in size. The tetrahedral rotation α, like octahedral distortion δ, are close to 0 degrees. Generally, the structure of Cs-ferriannite is quite relaxed and undistorted. The structure of Cs-annite could only be refined from powder data by the Rietveld technique. Its α angle is 5.2 degree, and the structure is more distorted than that of Cs-ferriannite.

The unit-cell data of the Cs micas are as follows:

	Cs-ferriannite	Cs-annite
a, Å	5.487 (1)	5.413
b, Å	9.506 (2)	9.385
c, Å	10.826 (6)	10.821
β, °	99.83 (3)	99.61

The cell of Cs-ferriannite, the largest mica cell known to date, is apparently a consequence of the large interlayer cation, matched by the relatively large Fe^{3+} in tetrahedral coordination.

These two micas behave like stable crystallines phases that should be considered among candidates for fixation and storage of radioactive isotopes of Cs in its interlayer.

CHEMICAL TREND AND OPTICAL PROPERTIES IN VERY LOW-GRADE CHLORITES FROM THE MALÁGUIDE COMPLEX (BETIC CORDILLERAS, SPAIN)

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Very low-grade metamorphic chlorites, identified in Silurian to early Permo-Triassic sequences from the Maláguide Complex (Betic Cordilleras, Spain), show abnormal composition and optical properties. These chlorites, ascribed to the alpine metamorphic event, have been studied by means of: (i) optical microscopy and electron microprobe analyses (EMPA), (ii) scanning electron microscopy (SEM), (iii) X-ray diffraction (XRD) and (iv) transmission electron microscopy (TEM/AEM).

EMPA and AEM results indicate that all the analyzed chlorites show an excess of octahedral relative to tetrahedral Al, with variations ($dAl = Al^{VI}-Al^{IV}$) ranging from 0.16 to 1.15.

Permo-Triassic chlorites are characterized by homogeneous Fe/Fe+Mg contents (0.52-0.55) and some variations in both Si^{IV} (2.98-3.11 a.p.f.) and total Al (2.6-3.0 a.p.f.). The passage from Permo-Triassic to Paleozoic is marked by a decrease in both Al and Fe contents, whereas the chemical trend in Paleozoic rocks, at increasing depths, is characterized by (i) a continuous decrease of Si (from 3.12 to 2.68 a.p.f.), (ii) increase of total Al (from 2.33 to 2.90 a.p.f.) and (iii) increase in both Fe content (from 0.6 to 2.8 a.p.f.) and Fe/Fe+Mg ratio (from 0.2 to 0.65), these variations showing very good correlations.

Chlorites from the Paleozoic sequence are, in spite of their different Fe content, mostly colourless in thin section and display very low birrefringence (< 0.001) and frequent optic sign inversions within the single crystals. This feature permits us to draw the line of birrefringence = 0, with a lower slope than that determined by Hey (1955).

Chemical and optical anomalies in Maláguide chlorites cannot be related either to mixed-layering with other phyllosilicates, as suggested by Shau et al. (1990), or stacking disorder as pointed out by Craw & Jamieson (1984), since Ca+Na+K contents are < 0.05 a.p.f. and XRD results indicate the lack of stacking defects. The frequent presence of an excess of H_2O in the analyses and the octahedral occupancy (5.3-5.9 a.p.f.) point, according to the data by Deer et al. (1962), to possible replacements of Fe^{2+} by Fe^{3+}, a factor that probably determines the chemical anomalies (Foster 1962). Nevertheless, optical properties, in detail, appear scarcely influenced by the variations of total Fe or Fe/Fe+Mg ratio. On the contrary, simultaneous variations in both Al^{IV} (or Si^{IV}) and Al^{VI}, appear as the essential factors determining the optic sign.

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DEHYDROXYLATION OF CHLORITES: AN HTXRD, DTA-TG AND IR STUDY

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Very low-grade metamorphic chlorites filling veins in the Maláguide Paleozoic (Betic Cordilleras, Spain), showing anomalous optics and average composition $[Si_{2.65}\,Al_{1.35}\,O_{10}\,(OH)_8(Al_{1.54}Mg_{1.70}Fe_{2.68})$, have been selected to study the mechanism for dehydroxylation. The study has been carried out by means of high-temperature X-ray diffraction (HTXRD), differential thermal analysis (DTA), thermogravimetry (TG), and infrared spectroscopy (IR).

Heating chlorite from room temperature up to 500 °C originates a general dilatation of the structure, marked by the broadening of basal reflections and the shift of (001) reflection from 14.33 to 14.43 Å. Between 500 and 900 °C, a set of changes in both intensity and position of the (00*l*) reflections, especially evident in the range 530-730 °C are observed, which can be summarized as follow: (a) Range 510-560 °C: Marked decrease of the intensity of the (002), (003) and (004) reflections, accompanied by a broadening of these, and gradual increase of the (001) reflection. (b) Range 560-620 °C: Notable increase of the intensity and simultaneous shift ($\Delta = -0.33$ Å) of the (001) reflection. (c) Range 620-730 °C: Gradual shift ($\Delta = -0.12$ Å) of the (00*l*) reflections and latter disappearence of the (00*l*) reflections other than (001). (d) Range 730-850 °C: Gradual decreasing and disappearence of the (001) reflection.

Three bands are present in the IR spectra of chlorite at 250 °C: A weak band at 3627 cm^{-1}, ascribed to inner hydroxyl groups, and two bands at 3569 and 3438 cm^{-1}, ascribed to the interlayer hydroxyl groups (Russel & Fraser 1994). From 520 °C, dehydroxylation is evident from both frequency shifts and decreasing intensities of the low-frequency bands. At 750 °C only the high-frequency band persists, which has shifted at 3656 cm^{-1}, and whose intensity gradually decreases until 800 °C.

DTA curves of these chlorites display a large endothermic peak at about 600 °C, and a weak exothermic effect at 825 °C. The endothermic peak is accounted for by the loss of the interlayer hydroxyls. The phase formed then is related to the 14.10 Å reflection. The absence of the non-basal reflections from this temperature indicates that the order in the ab plane appears to be lost, the new phase could be considered as a derivative from the chlorite with a partial disruption of its structure. The microanalysis (AEM) of this new phase is identical to that of the pristine chlorite, thus proving the absence of any diffusivity of ions outside the crystals. By contrast, the loss of the inner hydroxyls occurs gradually from 630 °C, as revealed by the TG curves and IR spectra. This loss induces a slight shift of the (001) reflection and is accounted for by the formation of the new 13.9 Å reflection. The increasing disorder from 670 °C is marked by the absence of the (00*l*) reflections other than (001).

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KAOLINITE-GROUP MINERALS FROM THE HYDROTHERMAL MERCURY DEPOSIT RÁKOŠ (CENTRAL SLOVAKIA)

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For the present the closed mercury deposit Rákoš is situated in the Permian clastic and low-metamorphosed sedimentary rocks in the SW part of the Spišsko-gemerské rudohorie Mts.

There were distinguished several types of ore mineralization: siderite veins with Cu-sulphides, siderite concretions, mercury mineralization (cinnabar in quartz-carbonate-barite veins) and oxidation zone. In the oxidation zone, halloyzite and allophane as a product of hypergene processes are present. The other ore mineral assemblages are accompanied by veinlets and cavities filled only by soft white kaolinite ± dickite. In mercury mineralized tectonic zone (thickness up to 40 cm) occur kaolinite-group minerals with illite, quartz, muskovite, tourmaline and pyrite.

On the basis of X-ray powder diffraction patterns, SEM studies, DTA and TG thermal experiments and chemical analyses (AES-ICP, AAS and spectrochemical methods) we can formulate following results:

— powder diffraction data confirm presence of the kaolinite polymorphs: well ordered kaolinite (corresponding to 1T polytype) and dickite, or mixtures of both;

— SEM-micrographs show two morphologically distinct types of kaolinite mineral phases: the book-shaped aggregates and euhedral crystals with dominant {100}, {001} and {110} crystal forms;

— analysed samples contain dioctahedral cations only, minor ammounts of trioctahedral cations and slight excess of silicon per formula unit can be considered only as influence of inpurities.

On the basis of the textural and fabric features, as well as experimental results, we propose the hydrothermal origin of the kaolinite polymorphs.

STUDY ON THE USE OF SLOVAK NATURAL GLAUCONITIC SANDSTONES AND GLAUCONITE CONCENTRATES AS SORBENTS OF PETROLEUM POLLUTION

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Technological study of natural glauconitic sandstones from Cerová vrchovina Upland (Southern part of Central Slovakia) and glauconite concentrates was performed.

Glauconitic sandstones within Cerová vrchovina Upland are marine Miocene (Eggenburgian — Fiľakovo Formation) disintegrating sandstones with 3–11 % of glauconite in some places (gray-greenish layers). Marine sandstones were examined on glauconite content and 3 localities were selected and sampled for glauconite concentrates preparation.

Glauconite concentrates of four fractions were prepared, with the average content 70–90 % of "technical" glauconite.

Basic ion-exchange and sorption properties, sorption capacity of ^{137}Cs and ^{109}Cd as well as sorption capacity of NH_4^+, Pb^{2+}, Cd^{2+}, Sr^{2+}, Cs^+ and NO_3^- were studied on natural glauconitic sandstones and glauconite concentrates.

Water cleaning tests from petroleum pollution showed the most promising results. Tests under stationary (non-flowable) conditions with model water/petroleum emulsion (concentration of petroleum components in water was 108 mg/l, petroleum components were diesel, transmission oil and emulgator) confirmed following optimal input conditions and sorption results:

Sorbent	Sorbent/ Cleaned mixture	Cleaning time	Removal ratio
Glauconite concentrate	1 / 10	20 min.	> 99 %
Natural glauconitic sandstone	1 / 10	60 min.	89.9 %

Further study of glauconitic natural sandstone and glauconite concentrate was managed and flowable experimental device was used.

Natural glauconitic sandstones appeared not to be suitable sorbent for flowable device because of pressure problems connecting with inhomogeneities in natural rocks (silt content). Also color of cleaned mixture was affected by clay particles from natural sediment.

Sorption results of glauconite concentrate in flowable device (fraction 0.09–0.5 mm) were less useful than under stationary conditions. Reason is that any mechanical influence (mixing) causes abrasion of glauconite grains and glauconitic slurry originates. Most of sorption reactions take place within this slurry substance of glauconite. Such substance does not origin in flowable device.

Also possibilities of sorbent regeneration and detoxification were considered. Burning seems to be more appropriate way of petroleum removal from glauconitic sorbents than washing by organic detergents.

BEHAVIOUR OF POLYMERIC Al CATIONS DURING THE PILLARING-PROCESS

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The introduction of polymeric metal-oxo-hydroxo-cations into the interlayer space of smectites leads to the formation of pillared clays. In the case of aluminium cations it is known that different species — the uniform Keggin cation Al_{13} and the polymeric Al cations (Al_{poly}) with unknown structure — are able to build up such a thermally stable microporous material.

We investigated the behaviour of the Al_{poly} cations during the pillaring-process. A solution containing only these cations is obtained by reaction of metallic Al with hydrochloric acid.

Different montmorillonites with varying CEC (from 0.72 mval/g up to 1.06 mval/g) were treated with such a solution of Al_{poly}; to get a pillared clay the amount should be ≥ 2 mmol Al/CEC. In opposite to the circumstances observed for Al_{13} it was found that the amount of pillar Al increases with the starting amount of Al_{poly} in the the system. So it may be varied by the conditions of preparation. This observation leads to the assumption that the polymeric Al cations are not uniform particles, they may vary in size and charge. The cations with a lower average charge per Al are preferentially intercalated in the interlayer space of a smectite. So polymeric cations with a higher charge should be enriched in the solution remaining after the pillaring-process.

The aim of this work was to find out differences between these kinds of Al_{poly} particles. Because the intercalated amount of Al is held very tightly in the interlayer space and the clay matrix would prevent characterization of these species we decided to compare the Al_{poly} cations in the starting solution and in the solutions obtained after pillaring.

In a first step we used the streaming current technique. This method is known to determine the charge of colloids and particles by polyelectrolyte titration. In this way the average charge per Al was determined for the Al_{poly} in the starting solution to 0.458. For the solutions remaining after pillaring a value between 0.54 and 0.56 was achieved. This fact gives the direct evidence that there exist Al_{poly} species with different charge per Al.

Additionally the Al_{poly} salts got after freeze drying of the different solutions were investigated by means of ^{27}Al-NMR-spectroscopy (MAS-technique), infrared-spectroscopy, gelpermeation chromatography and ferronmethod. While it was not possible to observe differences using the ferronmethod, the other attempts give advices for structural differences. From ^{27}Al NMR spectra two different types of octahedrally coordinated Al could be distinguished for the Al_{poly} salts. In the IR-spectra differences as well as in the region of deformation vibrations as in the region of valence vibrations are observed. The results of gelpermeation chromatography lead to the conclusion that a greater amount of cations with higher size is present in the starting-Al_{poly} than in the Al_{poly} salts got from the solutions remaining after pillaring.

All these observations give evidence that pillaring of montmorillonites may cause a fractionation of Al_{poly} by preferred introduction of cations with lower charge and higher molecular size into the interlayer space.

INTERCALATION OF CYCLOPHOSPHATE ANIONS IN HYDROTALCITE-LIKE COMPOUNDS

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The development in cyclophosphate chemistry made progress in recent years. The interest was concentrated on the preparation and crystal-chemistry. Today many crystal structures are known for cyclohexa- up to cyclododecaphosphates (P6–P12). They are mainly influenced by coordination of the cation and the crystal water molecules.

In this investigation we wanted to prove whether cyclophosphate anions would be able to enter the interlayer space of hydrotalcite-like materials by exchanging the interlayer anions. The hydrotalcite-like compounds (LDH) were prepared in the NO_3^--form (d(003) = 8.6 Å) and treated with alkali cyclophosphate solutions. As checked by IR-spectroscopy (band about 1380 cm^{-1}) the anion exchange was complete in all cases. Additional bands were assigned to O–P–O and P–O–P stretching vibrations, especially the latter one is typical for the cyclophosphates. The cyclophosphate structure seems to be practically stable under these conditions. This observation can also be confirmed by chemical analysis. The molar ratio Al : P is about one for all samples.

The intercalation yielded products with expanded interlayer space, but a quite distinguishable behaviour was found in the X-ray diffraction pattern for different LDH's. In the case of the Mg-Al-LDH (molar ratio Mg : Al about 2) the basal spacings of the products increased with increasing ring size of the cyclophosphates (Fig. 1) from 9.2 Å for the cyclohexaphosphate (P6) up to 10.7 Å for the cyclododecaphosphate (P12). The decrease in intensity and broadening of the reflexes give advice for the formation of more disordered structures.

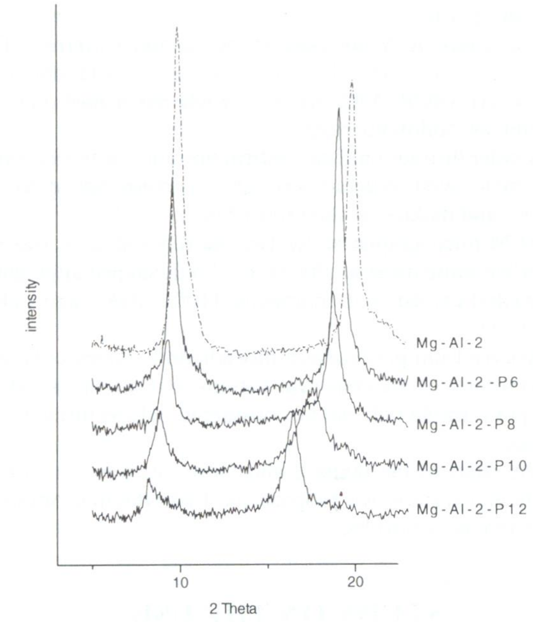

Fig. 1. X-ray diffraction pattern of Mg-Al-LDH compared with the cyclophosphate intercalates.

For the Zn-Al-LDH (molar ratio Zn : Al about 2.5) the intercalation products expose the same basal spacings about 9.2 Å, while for Zn-Cr- and Ni-Al-LDH's (molar ratio Zn : Cr and Ni : Al about 2) an inrease of the basal spacings was observed from P6 up to P10.

From ^{31}P NMR-spectroscopy (MAS-technique) it was observed, that the cyclophosphate structure is really essentially stable. The chemical shift of the cyclophosphates lies in the region of $\sigma = -24$ ppm. In the case of cyclododecaphosphate we observed distinctly the formation of a little amount of mono- and diphosphates ($\sigma = -2$ and -5 ppm, respectively) due to hydrolysis.

KAOLIN DEPOSITS OF SERBIA

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Most of the primary kaolin deposits in Serbia originated almost exclusively as a result of weathering of granite rocks — the Beli Majdan deposit on the Cer Mountain, the Garaši deposit on the Bukulja Mountain and Gornje Karačevo (the Bujanovac Granite Massif). However, there are several kaolin deposits of undefined genesis, which were formed either by weathering or by hydrothermal alteration — the Živkovci deposit on the Bukulja Mountain, Vrtogoš and Samoljica in the Bujanovac Granite Massif. Kaolins from the deposits of the weathering crust and the Živkovci deposit have been studied, as well as kaolin sand from the Pločnik deposit (which is located on the northern slopes of the Bukulja Mountain).

In this paper the geological characteristics of deposits are presented, as well as their mineral and chemical composition and basic technological properties. The genesis of kaolins is also discussed, and the influence of parent rock composition and the zonality of the weathering crust on the kaolin composition.

GEOLOGY AND MINERALOGY OF CERAMIC CLAY DEPOSITS IN WESTERN SERBIA

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Numerous deposits and occurrences of ceramic clays were found and explored in Western Serbia, along the border of the Pannonian Basin and Paleozoic basement. Ceramic clay deposits are located in three separated area: Jadarska Lešnica, Donje Crniljevo and Slatina. We have studied clays of the Donje Crniljevo area, since this has the most important clay pits: Jovanovića Brdo, Matića Brdo and Bele Vode.

All these deposits are of sedimentary origin, formed as the result of erosion and sedimentation of the older weathering crust on sandstones. Ceramic clays usually occur as tabular and lenticular bodies, somewhere up to 15 m thick. In their mineral composition kaolinite, illite and quartz dominate, accompanied by different, but generally minor amounts of feldspars. But the most interesting feature of these clays is the presence of substantial quantities of interstratified clay mineral — illite-smectite and, most probably smectite.

Clay minerals in the Donje Crniljevo area have been formed by the alteration of feldspathic and micaceous sandstone of the Devonian and Carboniferous age. Unfortunately, no primary kaolin deposits were found in that area yet, so the process of their alteration cannot be studied.

AB INITIO PERIODIC HARTREE-FOCK STUDY OF LIZARDITE 1T

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The trioctahedral 1 : 1 layer silicate lizardite, with ideal chemical composition $Mg_3Si_2O_5(OH)_4$, is interesting from the viewpoint of theoretical chemistry. The structure consists of two-dimensional sheets held together by weak forces along the (*c*) axis and provides an excellent case study of three types of coexisting chemical bonds: strong covalent bonds between Si and O in the tetrahedral sheet, ionic bonds between Mg and O in the octahedral sheet, and, rather weak hydrogen bonds fixing the individual 1 : 1 layers. However, most previous analyses of hydrogen bonding in lizardite have been supported by indirect evidence such as O-H...H distances or by the expected similarity of Si-O and Mg-O bonds in lizardite to analogous compounds treated by quantum chemical methods, e.g. MgO, brucite, $MgSiO_3$ or kaolinite.

The aim of this study is first to characterize presence the three types of bonding in lizardite by theoretical ab initio calculation, and to describe the electronic structure of the mineral in several important regions of the unit cell.

A periodic ab initio Hartree-Fock LCAO study was carried out on the 1 : 1 sheet silicate lizardite, $Mg_3Si_2O_5(OH)_4$, possessing P31*m* symmetry. A total of 258 atomic orbitals were described using double zeta quality basis sets argumented with polarization *d*(Si, Mg, O) and *p*(H) functions, respectively. Density of states and electron charge density maps were calculated to investigate the electronic properties. The majority of the valence states are composed of O and Si atomic orbitals with little contributions from H atoms. Calculations showed that while there are about $0.5|e|$ in Si(*d*) and about $0.1|e|$ in Mg(*d*) orbitals, the population of O(*d*) is negligible. The maps of charge density proved interlayer hydrogen bonds fix adjacent 1 : 1 layers. Positions of the main O peaks in projected density of states evaluated for both 3D and 2D calculations were influenced by layer-to-layer interactions, especially hydrogen bonds.

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CLAY MINERALS OF SEALS OF THE LOWER-MIDDLE JURASSIC OIL-BEARING DEPOSITS OF THE NYUROLKA DEPRESSION (WEST SIBERIAN PLATE)

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Lower-Middle Jurassic deposits are widely distributed within the West Siberian Plate. These deposits are of interest for the scientists not only from the point of view of understanding depositional and post-depositional processes, but also in relation to the recent discoveries of large hydrocarbon accumulations in them, particularly, the giant Talin zone of oil and gas accumulation. Special attention is paid to the Togur Formation which is not only a seal, a regional marker for the Jurassic deposits of West Siberia, but also has a high oil-generative potential.

The investigation of the substance composition of the clays was performed using the X-ray method. In addition, optic and electron microscopy, IR-spectroscopy, thermal analysis were also used. The objective of the investigation was the material from 9 wells in the eastern part of the Nyurolka depression. Four petrographic types have been distinguished among the argillites of the Togur Formation: 1 — black, coaly; 2 — grey tuffaceous; 3 — grey laminated with evidence of depositional deformations; 4 — brown-grey with shelly fracture. The set of clay minerals is similar in the first three types of argillites: this is a dioctahedral mica of muscovite type, rather well crystallized (from 40 to 70 %), kaolinite of a medium, sometimes low structural ordering (from 20 to 50 %), 14 Å-chlorite from 5 to 10 %, sometimes a mixed-layer mineral illite/smectite (d_{001} = 10.5 Å) is found in minor amounts. In grey tuffaceous argillites the roentgenoamorphous component (volcanic glass) is considerable, and mixed-layer minerals are slightly more important. The fourth type of argillites (Salat prospect) is notable for a peculiar clay substance: they are dominated by kaolinite to 60 %, mica in association with illite/smectite to 30 %, and the berthierine — 7Å-mineral with a serpentine-like structure and the composition identical to ferruginous chlorite to 15 %.

All of the above types of argillites have been also distinguished among the sub-Togur clays (Pliensbachian), separated from the Togur member by the sand horizon J_{16}. Most of them have the following ratios of clay minerals: mica is about 50 %, kaolinite — about 20-30 %, chlorite — about 10-20 %. The fourth type of argillites (Salat prospect) is characterized by a high kaolinite content of up 80 %, presence of berthierine and mica with illite/smectite.

The above-Togur argillites (Upper Toarcian) separated from the Togur Formation by a sand horizon J_{15}, are composed of the equal quantities of well-crystallized mica and kaolinite with a low degree of structural ordering. Chlorite and illite/smectite are present in minor amounts.

Thus, the detailed study of the Togur, sub-Togur and above-Togur clays has revealed the similarity of their polymictic composition over a significant territory of the Nyurolka depression. The inheritance of the depositional environments over the entire basin may testify to a moderate tectonic regime and stable source areas.

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ILLITE/SMECTITE AS A PALEOTHERMOMETER

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The reaction of smectite towards illite is quite unique among mineral diagenetic reactions. It is ubiquitous, because smectite is one of the most common weathering products. It is not restricted to a temperature range but advances continuously throughout diagenesis and anchimetamorphism. The reaction progress manifests itself as an increasing illite : smectite ratio in mixed-layer illite/smectite and it can be quantified using XRD, since Reynolds & Hower (1970) published a computer technique for simulation of XRD patterns of illite/smectites. These characteristics render illite/smectite a valuable source of information on the evolution of sedimentary basins.

Studies of shales from numerous sedimentary basins published over the last 25 years documented the shape of smectite illitization curves (% smectite vs. depth) similar to the one originally recorded for the Gulf Coast wells: decrease in % S starting rapidly at a certain depth (2-3 km) and then the rate of decrease gradually diminishing with depth. However, the curves were not identical and major differences in the slopes of the curve and in the depth of occurrence of the characteristic points (like for example R0/R1 and R1/R > 1 transitions) were observed.

Two alternative interpretations of the smectite illitization curve were offered by Hower and his students and the dispute started by them is still alive. Eberl & Hower (1976) opened the discussion by stating that their laboratory data on the illitization reaction kinetics do not allow us to discriminate between the kinetic and the thermodynamic control of the smectite illitization curve. Their followers were not so cautious. At least four alternative kinetic models for smectite-to-illite conversion have been proposed (McCubbin & Patton 1981; Pytte 1982; Velde & Vasseur 1992; Huang et al. 1993) and they are currently used for modelling the experimental data. Elliot (1995) tested the models on four different basins and concluded that none of them can be applied universally. Small (1995) reported that buffering the smectite illitization reaction with calcite increases the reaction rate by four orders of magnitude. This result questions all experimentally derived parameters used in kinetic models.

The alternative interpretation started by Hoffman & Hower (1979) and continued by Pollastro (1993) implies that the reaction rate is so fast that the illitization curve represents an approach to equilibrium, i.e., that % S·is controlled by the maximum paleotemperature experienced by the rock and, consequently, that % S can be used to evaluate these paleotemperatures. This model seems to be supported by the analysis of available field data from the Pleistocene to Proterozoic if only the cases with known basin histories are taken into account (Środoń 1995). It appears that the observed variations in % S vs. present day temperature can be explained not necesserily by the kinetic effects but by such factors as erosion or changes in geothermal gradient. K-Ar ages of illite/smectite from bentonites from the East Slovak Basin are also consistent with the equilibrium model (Clauer et al. submitted). The present author arrived at the following estimates of the temperatures corresponding to characteristic points of the illitization curve: the beginning of measurable illitization at 70 °C, R0/R1 transition (ca. 40 % S) at 120 °C and R1/R > 1 transition (ca. 15 % S) at 165 °C. This model should be further tested, using precise % S data from basins with well known and simple burial histories.

It is assumed that the equilibrium model applies only to shales, i.e., to closed systems containing excess K^+. In K^+-deficient environments, like thick bentonite beds, illitization is kinetically controlled, but the limiting factor is not the reaction rate but the rate of diffusion of K into impermeable bentonite beds (Altaner et al. 1984). In open systems, like sandstone beds, the illite/smectite composition may not be related to the regional thermal regime but it may reflect the temperature of migrating fluids, as documented by Whitney & Northrop (1987).

The illitization curves have been compared in numerous publications with different indicators of organic diagenesis like vitrinite reflectance or T_{MAX} curves, which are also used for the paleotemperature analysis by means of numerous kinetic models. No unique relationship exists between the two, although the trends are always parallel.

THE ELECTRON-OPTICAL INVESTIGATION AND BEAM MICROANALYSIS OF ANTIGORITE FROM THE MAGNESITE-TALC DEPOSIT AT HNÚŠŤA-MÚTNIK

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The occurrence of antigorite in the magnesite-talc deposit at Hnúšťa-Mútnik in the Spišsko-gemerské rudohorie Mts. with other magnesium clay minerals (sepiolite, palygorskite, saponite) and their assemblages in surrounding metamorphosed rocks was presented and confirmed by Turan & Turanová (1994).

More detailed morphological investigation of various samples of antigorite in water suspension under TEM Tesla BS 242 allowed identification of the following known shapes: chaotic or random arrangement (orientation) of fine lathy to tabular crystals with parallel attitude.

An electron microphotograph of the original sample of antigorite displays an irregular aggregate of minutely intergrown and parallely arranged crystals with sharp edges. Plane-parallel and fan-like, flaky to thin tabular distribution of ribbon-shaped to lathy antigorite crystals were observed in all cases. Electron micrographs confirm the slight difference in morphology of particles and antigorite was crystallized as a well developed tabular-shaped mineral.

The ascertained data about the morphological characteristic of antigorite correspond to published data by Beutelspacher et al. (1969), Gard (1971), Hovorka et al. (1983) whose micrographs show well-formed tabular-shaped crystals with sharp edges, perfect parallel growth and fragments of particles more or less strongly bound to aggregates and irregularly broken at their ends.

With X-ray-electron WDX quantitative microanalysis (JEOL JXA-840A; Kevex, Sesame software) was determined composition of antigorite: SiO_2 = 43.4 %; MgO = 42.1 %.

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CARBONIFEROUS CLAYEY ROCKS OF THE LUBLIN COAL BASIN AND THE POSSIBILITIES OF THEIR UTILIZATION IN CERAMICS

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In Poland bituminous coal deposits occur in three coal basins. The newest region of coal exploitation is the Lublin Coal Basin. Compared to other regions rocks of productive Carboniferous series (westfal) of Lublin Coal Basin are rich in clayey rocks. The rocks occur both in the roof and in the floor of the coal layer; they also form interlayers in it. During the coal exploitation the accompanying clayey rocks are being excavated to the surface and stored at the colliery dump. From the point of view of the mining activity, the rocks form wastes (after separation from the coal), but for some branches of the ceramic industry (e.g. building ceramics, cement industry) they may be a new basis of important raw materials.

On the basis of petrographic studies, it follows that the rocks are represented by claystones and clay shales (often rich in organic matter to the great extent), tonsteins, mudstones as well as — rarely — by fine-grained sandstones and clayey siderites. The dominant mineral component of claystones and clay shales is kaolinite. Illite and minerals of the montmorillonite-chlorite group occur as an admixture. The other components of the rocks are: quartz and organic matter.

The indicative chemical analyses of the rocks studied are as follows: SiO_2 — 49-68 wt. %, Al_2O_3 — 23-40 wt. %. The loss of ignition of clayey rocks from the roof and the floor of layers amounts to 9-25 wt. % whereas from the interlayers — 27-50 wt. %.

Thermal studies and technological tests point out that after firing of claystones and clay shales at temperatures above 1000 °C one can obtain ceramic bodies, which — according to the Polish standards — meet requirements for common brick products, and — in some cases — clinker bricks.

The industrial utilization of the clayey rocks accompanying bituminous coal of the Lublin Coal Basin allows — to the great extent — for the decreasing of the degradation of the natural environment.

EFFECTS OF IRON OXIDATION STATE ON CLAY-HERBICIDE INTERACTIONS

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The interaction of herbicides Atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine) and Alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)-acetamide) with ferruginous smectite (SWa-1) under different oxidation states was studied using batch equilibrium, membrane transport, and high pressure liquid chromatography (HPLC) techniques. Concentrations of both Atrazine and Alachlor decreased upon interaction with reduced clay, whereas the effect of oxidized clay was much less. When Alachlor was reacted with reoxidized clay, the effect was slightly greater than with the oxidized clay; but with Atrazine no discernible difference was observed between oxidized and reoxidized samples. HPLC patterns revealed a number of new peaks after reaction with reduced clays, indicating that degradation of the Atrazine and Alachlor had occurred; but the intensities of these peaks failed to account for all of the loss of the herbicide from solution, so adsorption or some other form of sequestration in the clay also occurs. In the case of Atrazine, degradation probably is the dominant process, but for Alachlor ancillary processes must also be involved and may be more dominant than degradation.

SYNTHETIC AMMONIUM ILLITE

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Ammonium illites were synthesized by hydrothermal alteration from an amorphous starting material of illitic composition. The starting materials, made from colloidal silica, aluminium hydroxide and ammonium hydroxide were used for experiments as a gel or glass (gel calcinated at 700 °C). Experiments were conducted in autoclaves at 300 °C. The reaction times ranged from 3 hours to 4 weeks. The reaction products were characterized using X-ray diffraction, high resolution electron microscopy and IR spectroscopy.

The results show significant differences between hydrothermal reactions made on gel and glass. Illite formation from gel was very fast. Even after a 3 hour treatment, a small diffuse 001 illite reflection appeared in an XRD pattern. Within 24 hours, characteristic illite XRD patterns appeared and transformation of the three-dimensional Si-framework to layered structure was confirmed by the shift of Si-O stretching band from 1109 to 1026 cm^{-1} in IR spectra. No other significant changes were noticed by XRD an IR in the interval between 24 hours and 4 weeks. HRTEM images show increase in number of 2 : 1 layers per one crystal and different distributions of crystal thickness indicating changes in the crystal growth. Hydrothermal reaction of the glass was completely different. The only phase determined by XRD within the first week was randomly interstratified NH_4-illite/smectite with expandability 90 %. Next two weeks run lead decrease of smectite portion in mixed-layer mineral (70 %). Three and four weeks of treatment give the same result — increase of illite/smectite expandability and origin of ammonium illite as a new non expanding mineral phase.

PYROPHYLLITE FROM TWO SLOVAK VOLCANIC REGIONS: DISTRIBUTION AND MINERALOGY

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Distribution of pyrophyllite and other clay minerals was studied in quartzite quarry in Šobov (near Banská Štiavnica in Central Slovakia) as the first step of our work. Pyrophyllite was determined in 21 samples and illite in 48 samples (from 61) by X-ray diffraction analysis. Obtained distribution shows significant differences. Argilic rocks with pyrophyllite and illite were found in left part and quartzite in right part of quarry.

Pyrophyllite and illite appeared in same period depending on local conditions: lower pH was advantageous for origin of pyrophyllite and higher concentration of potassium for illite. Aluminium, important for origin of pyrophyllite, came from original andesite that was alterated by acid fluids from granodioricor dioritic intrusions.

Mineralogical properties of pyrophyllite (L26) from the Šobov quarry were compared with those of pyrophyllite (VH) from Vígľašská Huta hydrothermal deposit (Javorie Mts. in the Central Slovakia). Structural formulas of both samples are almost same. Shape and particle size of pyrophyllites seem to be approximate by same. This was determined by TEM. Sample VH represents triclinic polytype and polytype determination of the sample L26 was not successful according to Brindley & Wardle (1970). Higher stacking order of pyrophyllite from Vígľašská Huta was indicated by IR spectroscopy (sample L26 has only one diffuse vibration in area of Si-O stretching vibration) and computer program MudMaster (Eberl et al. 1996). Program calculated that thickness of XRD scattering domain of sample VH was larger (17.5 nm) than for L26 (8.3 nm). Higher stacking order of sample VH is probably due to more constant origin conditions of pyrophyllite.

Properties of natural pyrophyllite were modified by grinding and calcination. Samples were first ground for 3 and 6 hours. XRD patterns show significant decrease of pyrophylite reflections accompanying structural changes. Reflections of quartz remained stable within the grinding. Weak reflections of mullite were obtained after 3 hours of grinding, they were more expressive after 6 hours. Quartz was almost the only mineral phase shown after grinding of samples for 1 hour and heated to 900 °C. Small reflection of mullite also appeared. Cristobalite was originated by heating of the same sample to 1000 °C. Reflection of mullite was brightly visible and quartz still remained in the sample. Quartz disappeared after the heating to 1100 °C. Reflections of mullite and cristobalite were clear and well defined.

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A COMPARATIVE STUDY OF THE SORPTION PROPERTIES OF BENTONITES FROM BULGARIAN DEPOSITS

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The enlargement of the adsorption process utilization areas has resulted in thorough studies of the used sorbents (active carbon, silicagel, etc.) and designs for new materials with molecular-sieve and other specific properties.

The good adsorption, catalytic and ion-exchange properties of the clay minerals, the creation of effective methods for regulation of the structure and chemical nature of their surfase, together with the fact that they form big deposits convert these minerals into economically valuable materials which can be utilized in a number of technological processes.

Two main reasons determine the cation-exchange capacity of the clay minerals: 1 — Replacement of Si^{4+} with Al^{3+} in the structure and of Al^{3+} with a lower charge (mostly Mg^{2+}). This leads to creation of a negative charge in the structure. 2 — The breaking of the chemical bonds in the crystal structure of the clay minerals leads to the formation of OH^- groups. The hydrogen from this group can participate in exchange reactions under certain conditions.

Six samples from monmorillonite clays were used in the experiments. Four of them were not treated at all, one was activated by heating, and one was acid-treated. For ion-exchange capacity determination all samples were treated with 1.0 N solution of NH_4Cl in the same conditions.

The result showed that the "white" monmorillonite clays have a higher sorption capacity than the "yelow" and "blue" bentonite. It is quite interesting that the "white" monmorillonite clay shows better sorption properties even compared with the acid-activated bentonites. This may be a result of interpreted due to the greater quantity of cristobalite in these samples.

CLAY MINERALOGY ASPECTS OF THE ALGINITE CASE STUDY OF THE ALGINITE AT PINCINÁ, S. SLOVAKIA

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Late Miocene basaltic volcanic activity at the Southern Slovakia originated Podrečany Basalt Formation. In frame of the formation there are many volcanic forms including maars. Central part of a maar situated near the vilage Pinciná (NE of the town Lučenec) is filled by the alginite. Alginite is a clayey sedimentary rock composed by pelitic material washed down to the maar lake from weathered basalt mostly lapilli tuff from which the maar ring is built. Alginite is rich in organic matter of the Algae origin.

The yellow-green Algae, particularly of the taxa *Botriococcus braunii* found very convenient life condition in the upper layer of the maar lake water. Colonies of Algae after death sunk down to the lake bottom to be buried by pelitic material. Because of the anaerobic conditions at the lake floor the Algae organic matter did not undergo the disintegration and is well preserved in a high content (average TOC content about 9 %, average humus content about 15 %).

The main clay minerals of alginite are illite and kaolinite accompanied by smectite. Due to the smectite but also due to high content of the well preserved organic matter the alginite has some exceptional qualities. First of all it is a great surface area (313-654 m^2/g) and as result of it the high water absorption capacity (74.14-160.94 wt. %, average 110.66 wt. %). The alginite is capable to detain the heavy metals, especially the lead. At the proportion 1 kg of sorbent (alginite)/1 m^3 water contamined by lead in the quantity not higher as 5 mg/l the alginite is able detain up to 98 % of the lead.

Because the anorganic compound of the alginite is the pelitic material originated by basaltic tuff weathering, the alginite is rich in nutrient elements. This circumstance, as well as the high content of humus fits well for agricultural soil amelioration. Beside to give the nutrients, and to restore the soil structure the alginite protects the soil against the desication during the drought periode, prevents the leaching of the nutrients from the soil and significantly hiders the ground and superficial water polution by the nitrates, phosphorus and potassium.

ROLE OF CLAY MINERALS IN ENVIRONMENT PROBLEMS

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The environment is a new frontier which has only been partially explored, also as regarding methods of analysis. These must be reconciled by interdisciplinary approaches in order to achieve both knowledge and wisdom.

The problems dealing with environment impact may have various objectives: air and water pollution, soil contamination and urban industrial-nuclear wastes, their by- products and reuse, land reclamation and new settlements, surface and underground facilities, man-made reservoirs and dams, exploitation of mineral resources and quarry-mine restauration, harnessing of oil-gas and water reservoirs, subsidence, etc. These many aspects are involving different branches of fundamental and applied research, such as environmental and engineering geology, soil mechanics, hydrogeology, agriculture, human health, etc.

"Argillology" is certainly a specialized branch of investigation in these fields.

Soil and clay sediments cover more than 80 % of the Earth's surface. Recent experiences have clearly indicate that control and modification of clay component properties may give more precise information toward better understanding, and for solving environmental problems fairly well defined. Due to their common availability and peculiar properties (fineness, high surface area, reactivity and polarity) natural and modified clay minerals are materials potentially involved in many processes and mechanisms (sorption-release, dispersion-flocculation, swellings-shrinking, spatial architecture of solid particles and interstitial pore size-shape, etc.) which are leading the physico-chemical behaviour of soils, fluid flow, air-water suspended particulate, etc.; thus, playing an important role in environmental research. Certain clays represent an environmental danger (geochemical concentration of poisonous elements, landslides, stone decay, etc.), but others can also be positively used (clay "engineering") for manufacturing new products.

Amount and type of clay minerals, ill-crystallized or amorphous coating on solid particles, associated organic matter and/or other cementing precipitates are facets of a complex issue: no two clays are identical, even with similar mineralogical and chemical composition! Simplified models and the avoidance of seemingly minor factors might lead to erroneous conclusions and dreadful consequences in seeking effective remediation technologies. A better understanding of surface assisted chemical reactions is urgently needed for a more through assessment and prediction of the behaviour of chemicals in natural systems: the study of long-term behaviour of clays is not an option, but a necessity. Interactions in clay-electrolyte aqueous solutions, clay-heavy metals-organic substance complexes, surface and ground water pollution, soil and waste management, transport and diffusion of radionuclide colloids, soil instability and consolidation-stabilization treatments are fundamental topics to help clarify the meaning of "environmental argillology" and its importance in determining remedial measures to be applied for the conservation and improvement of environmental quality.

Argillology should be a key component right from the beginning of most studies dealing with management of the environment, and clay specialists should be called on to participate in the decision taken. An underevaluation of the consequences of inadeguate attention to perspective problems is also the most immediate causes of the present difficulties in dealing with public opinion regarding the real or presumed danger of man's encroachment of the environment. Ignoring it can result only in a "fight against wind mills".

Several case-histories of past and current events occurred in Italy, which had also worldwide repercussions, and results of investigations carried out by the team for clay research working in our Department in collaboration with the National Authority for Environment (ENEA), will be presented:

— subsidence in the Po delta and the danger of Venice flooding;

— landslides in Apennines areas, and the catastrophic and tragic Vajont dam landslide occurred in 1963;

— instability of clayey subsoil due to seeping of urban sewages of historical cities (Orvieto, Civita) in Central Italy;

— water pollution in rivers and along the coastal shelves of Italy.

CLAY MINERALOGY OF BARREN ROCKS IN THE LOWER MIOCENE BROWN COAL DEPOSITS OF THE BORSOD BASIN (N. HUNGARY)

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Detailed sampling was carried out in 14 coal seam profiles of 7 brown coal occurrences in the North Hungarian Borsod Basin. The mineralogical analysis was part of a complex study aiming to reconstruct the paleo-environmental relations of the deposition of the Ottnangian coal sequence.

The samples and the < 2 μm fraction were analysed by X-ray diffraction. DTA-DTG methods were used to determine the organic carbon and total carbonate contents of the bulk samples and to characterize the water contents and adsorbed cations in clay minerals (M. Földvári, Zs. Barna).

In the lower stratigraphic position within the coal sequence the dominant component of the underlying and interlayer formations of the coal seams is redeposited volcanogenic material. Volcanogenic components are derived from local sources such as from the Ottnangian "Gyulakeszi" rhyolite tuff and from the products of its terrestrial weathering which form the base of the coal sequence. The clay, carbonaceous clay and bentonite layers within the coal seams contain plagioclase, partly of high temperature modification, little clinoptilolite, much smectite with predominantly Na cation, little illite and various amounts of kaolinite/smectite mixed-layers or disordered kaolinite. The transformation of the acid volcanic glass and feldspars into smectite and the subsequent transformation of smectite into kaolinite is accompanied by the production of amorphous silica and the precipitation of opal-CT, cristobalite or quartz resulting in diatomaceous and silicified coals. The rocks are practically carbonate-free and contain little detrital quartz.

There are few bentonite layers identified in wide areas that are derived from synchronous fallout of acid tuffs. These tuff layers are usually less kaolinized than the redeposited ones.

In the higher stratigraphic horizons and in the overlying formations of every coal seam the dominant components of the rocks are terrigeneous clastic sediments. They contain detrital quartz and feldspar, mixed-layer illite/smectites with high proportions of smectite (80 to 100 %), illite-2M, detrital chlorite and kaolinite. The terrigeneous clastic rocks usually contain calcite + dolomite (10 to 20 %).

As shown by the high smectite contents, disordered minerals and degree of coalification, no burial diagenesis or postdepositional thermal effect affected the coal deposits.

CLAY MINERALOGY OF SEDIMENTARY FORMATIONS CONTAINING MICROSPHERULES AND OTHER SUBSTANCES OF COSMIC ORIGIN

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The possible role of clay mineralogy in the study of rocks enclosing substances of cosmic or impact origin is reviewed. This study is in connection with a new IGCP Correlation Programme No. 384 "Impact and Extraterrestrial Spherules" starting in 1996.

In cosmic matter (meteorites, rocks of the Moon) clay minerals, even hydrous layer silicates are extremely rare (very minor amounts in some Apollo 11 lunar samples and in carbonaceous chondrites). The hydrous layer silicate serpentine is relatively abundant in the zone of asteroids and among the satellites of the planets Jupiter and Saturn.

The non-sedimentary, first phase products (suevites) of the impact crater contain fresh glassy components. Clay mineral formation starts first during the subsequent post-impact sedimentary history. Examples are given from the Miocene crater lake of the Ries structure at Nördlingen, Germany, the Cretaceous/Tertiary boundary layers in a peat-forming environment of western North America, marine deposits of the Eastern Alps and Jurassic/Cretaceous boundary formations near an impact structure in the Barents Sea.

Mineralogical analysis may contribute to the reconstruction of the conditions of sedimentation, alteration and diagenesis of rocks containing cosmic or impact-derived substances. Examples from the study of Hungarian sedimentary formations containing spherules:

Lower Anisian Vöröshegy Dolomite Member in the Mecsek Mts. Transition between two clay mineral associations: The lower one is illite + Mg-chlorite + corrensite formed in a restricted basin environment, the upper one is detrital illite typical of shallow marine sedimentation.

Upper Cretaceous of the Bakony Mts. Microspherules were found in alluvial sediments of the non-marine siltstones, clays and variegated clays of the Csehbánya Formation as well as in the Ajka Coal Formation and in the marine Polány Marl Formation. According to clay mineral analyses non-marine formations and clastic intercalations of the Ajka Coal Formation are characterized by the detrital association of illite+chlorite or by the association of very disordered smectite, illite/smectite, illite and chlorite. The marine beds of Polány Marl contain similar but well ordered phases.

Upper Pannonian (Pliocene) deposits in the Little Hungarian Plain. Detrital terrigeneous polymineralic clay mineral association of illite+chlorite in the bulk rock and highly expandable illite/smectite in the < 2 μm fraction.

No evidence of volcanogenic sedimentary components was found in these formations on the basis of the study of clay minerals.

EMISSION AND FIXATION OF F AND S IN CLAY BASED CERAMICS

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Clays are fundamental raw materials for structural ceramics. They might contain chemicals which are volatiles, such as: H_2O, F, S, Cl and P. These volatiles are located in mineral structures, either of clay minerals or of non-clay minerals.

Aveiro is a region where huge clay and sand deposits occur. From them large volumes of clay and sand are extracted in order to be used in the numerous ceramics plants dispersed throughout the region. These ceramic plants produce bricks, roof tiles, wall tiles and floor tiles.

Sampling had been carried out both on those ceramic raw materials and on their ceramic products. In regards with their chemical composition particular attention was paid to F and S taking into account their environmental impacts. Volatiles nature and content were determined using spectrophotometric and selective electrode methods.

The herein disclosed data is concerned with a local ceramics plant producing both brick and roof tile, whose mean overall production is estimated at 15,000 tons/month, 5,000 tons of roof tile and 10,000 tons of brick. Brick is fired at 910 °C whereas roof tile is fired at 985 °C. Raw materials formulation is the same for both products: 40 % Bustos clay + 60 % Aguada clay. To this mixture is added 13 % of Sosa sand. F and S contents in the final mixture were estimated at 0.34 % and 0.05 %, respectively.

F is hosted in clay minerals, replacing (OH) structural groups. Bustos clay, an illitic/smectitic clay, contains more F (0.65 %) than Aguada clay (0.30 %), an illitic/kaolinitic clay.

F average content for roof tiles was estimated at 0.022 %, whereas F average content for bricks was estimated at 0.030 %.

It is evident the large quantity, estimated at 45 tons/month of fluor emitted to the atmosphere.

S average content for roof tiles was estimated at 0.12 %, whereas S average content for bricks was estimated at 0.30 %.

S is hosted either in sulfates (gypsum, anhydrite and melanterite) or in sulphides (pyrite and marcassite) which have been identified in the clays.

Roof tiles and bricks fix a significative amount of S from the fuel (thick fuel oil containing 3.5 % S + gas propano) utilized in the ceramic plant.

Interpretation of the analytical results referred to is put forward, taking into account raw materials, ceramic products and fuel compositions as well as firing temperature, regime and residence time.

Experimental data related with fixation of F in the ceramic products using the addition of carbonates to raw materials mixture are disclosed also.

DISTORTIONS OF COORDINATION POLYHEDRA IN PHYLLOSILICATES AND THEIR INFLUENCE ON THE DIFFRACTION PATTERN

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Analysis of crystal structure data for 112 phyllosilicates (85 micas, 14 1:1 phyllosilicates and 13 chlorites) shows that the same principles govern the geometry of polyhedra and their sheets irrespective of the phyllosilicate subgroup. From the analysis of octahedral coordination it follows that all octahedra in the phyllosilicate structures are distorted and the degree of distortion can be described by octahedral flattening angle Ψ and counter-rotation angle δ of top and bottom anion triads. Regression relations for both Ψ an δ as a function of octahedral cation-anion bond length $d(M-A)$ are proposed. Both kinds of distortion of individual octahedra are a function of neighbouring octahedra and the nature of the edge-sharing topology of the octahedral sheet.

The tetrahedral sheet adjusts its lateral dimensions to those of the attached octahedral sheet by an in-plane rotation of tetrahedra such that adjacent tetrahedra rotate about **c*** in opposite senses. Regression relation for tetrahedral rotation angle α as a function of the mean basal tetrahedral edge length and the mean octahedral bond length $\bar{d}(M-A)$ was derived.

For a given chemical composition and a distribution of cations in the structure, the diffraction pattern of a phyllosilicate varies also with distortions of coordination polyhedra and their sheets. Measures of distortion can be used to generate atomic coordinates and these readily yields a calculated pattern. Calculations performed for various types of phyllosilicates show that the intensity distribution varies mostly with the tetrahedral rotation angle α, specifically for diffractions $20l$ ($13l$) (orthogonal indexing). Diffractions of the $02l$ ($11l$) type are subject to much less variation. The counter-rotation angle δ is generally less important as regards intensity. The flattening angle Ψ affects the intensities of basal diffractions.

TALC I. POLYTYPIC STRUCTURE AND SHAPE FACTOR ESTIMATION FROM XRD PATTERN

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Talc from Puebla de Lillo, Spain has been studied by XRD. The experimental X-ray powder diffraction patterns have been compared with the simulated diffractograms from structure refinements data for the triclinic and monoclinic talcs.

The series of diffraction patterns of monoclinic and triclinic talcs were calculated for differently oriented particles in aggregates ($g = 0, 1, 2, 3$). The results proved that the relative intensities are highly dependent on the g parameter, even for the very weakly textured samples. It has been also found that the texture modified relative intensities are evidently different for the two polytypic modifications.

The polytypism of talc is discussed. The X-ray results were compared with those obtained for other talc samples (Turkey, Egypt). The unground sample of talc from Puebla de Lillo studied here belongs to fine grained steatite, characterized by disordered structure. Due to random translations of the layers along the Y axis all the reflections of the $02l$ and $11l$ series (which correspond with YZ projection) are smeared out.

A "shape factor" was found helpful in the identification of polytype if a coefficient of orientation has been measured independently. It displays lower values for the triclinic polytype than for the monoclinic one for the same g value.

Talc from Puebla de Lillo was determined to belong to subfamily A. Indication of its monoclinic symmetry was derived from the comparison of the experimental and calculated diffractograms and from the "shape factor" determination.

ESTIMATION OF CHEMICAL COMPOSITION OF CHLORITES FROM $d_{(001)}$ AND b PARAMETERS

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The regression equations for b parameter were independently calculated for two populations of chlorite analyses.

For the trioctahedral chlorites, the equation, derived by analyzing 83 published chemical and structural data, is: $b(\text{Å}) = 9.22514 + 0.02698\ \text{Al}^{\text{IV}} - 0.03863\ \text{Al}^{\text{VI}} + 0.03761\ \text{Fe}^{2+} - 0.03760\ \text{Cr} + 0.06651\ \text{Mn}$. The composional variables are in numbers of atoms per half formula unit, i.e. $O_{10}(OH)_8$. Si^{4+} and Mg^{2+} contents are not taken as independent variables because they are collinear with other variables. Thus, the intercept value is common for talc-chlorite composition. For di-tri- and di-dioctahedral chlorite, the regression equation, based on 31 analyses, is: $b(\text{Å}) = 8.86020 + 0.11193\ \text{Al}^{\text{IV}} + 0.05238\ \text{Mg} + 0.07518\ \text{Fe}^{2+} + 0.05998\ \text{Fe}^{3+} - 0.05229\ \text{Li}$. Similarly, Si^{4+} and Al^{VI} were excluded from the list of variables due to their very high correlation with other variables. The intercept value is that of purely aluminous chlorite composition.

The classification diagrams of chlorites, with the plotted lines of the constant b and $d_{(001)}$ can be used for estimation the chemical composition of chlorites, basing on powder diffraction patterns. The lines of constant values of b and $d_{(001)}$ cross at wide angles, which diminishes errors of estimation. For lithium-bearing chlorites a separate diagram has been presented. Basing on the same diagrams it is also possible to estimate b and $d_{(001)}$ from chemical composition.

URANIUM IN KAOLINS AND CO-OCCURRING MINING WATERS OF SOME LOWER SILESIAN KAOLIN PITS (POLAND)

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In Poland the deposits of industrial kaolins are situated in Lower Silesia. Actually, a final product, that is, washed kaolin is obtained only from poorly compacted kaolinitic sandstone from the "Maria III" deposit in Nowogrodziec. On account of insufficient covering of domestic demand for washed kaolin (only ca. 40 %) the possibility of undertaking the exploitation of residual kaolin from "Antoni" deposit in Kalno nearby Swidnica is being considered.

The uranium content in some Lower Silesian kaolins is higher than the average in clayey rocks amounting to ca. 4.2 ppm. This fact has been stated, among others, for an example of kaolins and weakly kaolinized granites exploited quite recently from "Andrzej" open pit in Zarow. Some mining waters of this deposit are also characterized by an elevated content of this element. The similar situation should be expected at the undertaking of exploitation of neighbouring, "Antoni" kaolin deposit.

The uranium content in the studied samples from "Andrzej" open pit, determined by means of INAA (instrumental neutron activation analysis), amounts to:

— 37 ± 10 ppm — for weakly kaolinized granite,

— 11.3 ± 2.6 ppm — for residual kaolin.

It is possible that the reason for the elevated uranium content in these kaolins is the presence of uranium in minerals of pegmatite veins cutting the kaolinized granite of the "Andrzej" deposit. In the weathering process, uranium of some pegmatitic minerals undergoes the oxidation from U^{4+} to U^{6+} making mobile and perfectly soluble uranyl ion $[UO_2]^{2+}$. The above is the probable reason for the distinctly elevated content of uranium in the mining waters of "Andrzej" pit occurring in the direct neighbourhood of the kaolinized granite (for example ca. 0.5 ppm in samples collected during spring periods). The uranium content is changeable in different seasons of the year, nevertheless, it exceeds remarkably the concentration of this element in most ground waters. The range for the majority of them is from 5×10^{-12} to 5×10^{-9} mol $[UO_2]^{2+}$ per litre. Moreover, in summer time, especially in the very hot and rain-free period, when there the majority of mining waters dry up, one can observe the crystallization of secondary sulphate minerals (e.g. copiapite) in which a remarkable concentration of uranium ion exceeding 1 wt.% has been stated.

In contrast to "Andrzej" open pit, the uranium content in mining waters in the only actually exploited "Maria III" deposit is distinctly lower and does not exceed 0.2 ppm U, which is the uranium detection limit of the applied polarographic method.

INVESTIGATIONS OF ALUMINIUM EXTRACTION FROM CLAYS BY MEANS OF PHOSPHORIC ACID

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The investigations on obtaining aluminium oxide from non-bauxite aluminosilicate raw materials, using an acid method were carried out at the Institute of Chemistry, Inorganic Technology and Electrochemistry of the Silesian Technical University. The technological concept of the Al_2O_3 manufacturing process assumes a decomposition of clay minerals by orthophosphoric acid and connection of process with production of phosphatic fertilizers and building materials. Preliminary dephosphatizing of post-extraction acid solutions has been performed with ammonia water and the final one by means of roasted dolomite. The aluminium from dephosphatized post-extraction solutions has been leached with weak solutions of sodium hydroxide. Silica wastes have been investigated from the point of view of their possible use in the production of constructional binding materials, insulating materials and acid proof ceramics.

Investigations of aluminium extraction with phosphoric acid were performed on clays samples from actually exploited deposits (Jaroszów, Turoszów) as well as on flying ash from the power stations "Turów" and "Łaziska". Degree of aluminium leaching and kinetical characteristics of the process were investigated depending on temperature, the time of leaching, acid concentration, quantity of acid and pressure.

The positive effect of preliminary roasting of clays in the temperature of 600-800 °C on their decomposition with phosphoric acid has been stated. The optimum parameters of the process of aluminium extraction have been established. It has been found that in the determined optimum conditions the extraction efficiency reaches about 95 %.

TONSTEINS OF THE DONETS BASIN AS INDICATORS OF HUMID HOT CLIMATE DURING CARBONIFEROUS PEAT FORMATION AND SEDIMENTATION

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The goal of the research, that we carried out for a number of years, was to approach the solution of contradictory problems about the source of initial material, forms and transportation agents to peat bogs, their transformation conditions to rock-forming tonstein mineral — the kaolinite.

The materials were tonsteins found and studied by us in different parts of the carboniferous sequence (from suite C_1^3 lower to suite C_3^1 upper) and in different regions of the basin.

By a complex of macroscopically observed features, mode of occurrence and geological distribution tonsteins differ significantly from other rocks of coalbearing deposits. The crystalline texture of the majority is unique among ordinary clay rocks, which also allows us to undoubtedly distinguish them from other intercoal mineral layers. Complex crystal optics, chemical, thermal, roentgenometric and IR-spectrometric study showed that in hard coal development regions the tonsteins consist of kaolinite while in the anthracite development regions the tonsteins consist of kaolinite while in the anthracite development region their rockforming mineral is hydromica of muscovite (or paragonite) type, which we explain by a metagenesis (initial metamorphism) influence process. In tonsteins zircon, rutil, tourmalin, apatite, corundum, garnets are the only accessory minerals, while carbonates and iron disulphides are the only authigenic minerals.

To assess the genesis of tonsteins and determine their place among clay rocks we placed the average value of chemical composition (of 60 tonstein samples from 15 coal seams) by element groups (Al_2O_3 + TiO_2; SiO_2 + K_2O; CaO + MgO + FeO + Fe_2O_3 + Na_2O + loss during firing) onto a triangular diagram on the margins of which continental clay of humid hot and cold temperate climatic zones were marked. Such a diagram was borrowed from the work by Ronov & Khlebnikova (1957). Each point inside the diagram represents the results of individual analysis or the average value of a range of samples from a given tonstein. The position of these points on the diagram depends on the average content of each of the three groups of components mentioned above. As can be seen from the diagram, all tonsteins are grouped by chemical composition in the development zone of humid hot climate clays even in the upper part of this zone. In addition the low value of the silicon module (ratio $SiO_2 : Al_2O_3$) compared to pure kaolinite can imply the existence of free Al_2O_3 and in some tonsteins it was established experimentally (about 2-3 %). The Maturity coefficient by Pettijohn (1957) that is expressed by ratio $Al_2O_3 : Na_2O$, for tonsteins is rather high, more than 100.

Hence intercoal layers, i.e. tonsteins, characterized by relative enrichment of less mobile components (Al_2O_3, TiO_2), low content of mobile components and poor accessory minerals association represent products of deep chemical and biochemical initial aluminosilicate volcanogenic material transformation in carboniferous peat bogs. Thus it corresponds to "primary kaolin" which is formed in the same weathering count. This is why it indicates a humid hot climate in the Carboniferous period.

EVOLUTION OF HYDROTHERMAL ALTERATION PROCESSES IN THE BANSKÁ ŠTIAVNICA-HODRUŠA ORE DISTRICT: SPATIAL, TEMPORAL AND GENETIC ASPECTS

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The Štiavnica stratovolcano, hosting the rich Banská Štiavnica-Hodruša ore district, is the biggest volcano of the Carpathian-Pannonian region, involving a large caldera, resurgent horst and an extensive subvolcanic intrusive complex. Its evolution took place during the Early Badenian to Early Pannonian time (16.5 to 10.0 Ma) in seven definable stages:

1 — Formation of a large pyroxene/hornblende andesite stratovolcano with emplacement of andesite porphyry sills and laccoliths in the central zone during maturity of the volcano. Alterations at this stage were limited to "autometamorphic" chloritization and/or hematitization of intrusive rocks.

2 — Emplacement of a quartz-diorite intrusive body followed by evolution of a high-sulphidation hydrothermal system with extensive alteration of advanced argillic type — pure silica core surrounded by a zone of pyrophylite and pyrite replacement, grading outward into a zone with illite and propylitic assemblage.

3 — Emplacement of a large granodiorite bell-jar pluton in the basement. There are magnetite bearing skarns at contacts of granodiorite with carbonate rocks. A local hydrothermal system in the central part of the granodiorite pluton lead to formation of stockwork base metal mineralization accompanied by intense quartz, pyrophylite/kaolinite, illite, pyrite alterations in overlaying andesite complex.

4 — Emplacement of granodiorite/quartz-diorite porphyry stocks and dyke clusters around the granodiorite/diorite pluton. Hydrothermal systems related to individual stocks/dyke clusters gave rise to copper porphyry/skarn ore deposits with a typical alteration zoning — a weak potassic zone with secondary orthoclase and biotite in the center is surrounded by well developed phyllic zone with quartz, sericite, pyrite replacement, which grades outward into zone of propylitization. Advanced argillic zone with kaolinite, illite, quartz and pyrite has been mostly eroded.

5 — Caldera subsidence and its filling by sediments and biotite-hornblende andesites. Emplacement of quartz-diorite porphyry sills, ring dykes and dykes at subvolcanic level. Intrusion related (?) hydrothermal systems gave rise to hot-spring activity leading at several places to advance argillic alterations of high sulphidation type with quartz/opalite, kaolinite, pyrite and alunite (one locality only), grading downward into illite and/or smectite dominated association.

6 — Renewed activity of less differentiated andesites from dispersed centers on slopes of the volcano and along the caldera fault. Initial stage of the resurgent horst uplift.

7 — Uplift of the resurgent horst in the center of the caldera, accompanied by gradually increasing amount of rhyolites and granite emplaced along marginal faults of the horst. Interaction of an extensive, gradually cooling low sulphidation hydrothermal system with evolving structure of the horst has given rise to rich base and precious metal vein type mineralization with typical zoning. Mineralization is accompanied by extensive adularia/sericite alterations, grading outward from individual veins into propylitic zone.

Rocks in the Banská Štiavnica-Hodruša ore district are often affected by several stages of alteration. In intrusion related systems a high sulphidation initial stage (SO_2 rich low pH fluids) is usually followed by a medium to low sulphidation stage (SO_2 poor moderate pH fluids).

KAOLINITE-ALUNITE AND BENTONITE OCCURRENCE FROM DEKÝŠ (ŠTIAVNICA STRATOVOLCANO)

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A more specific data on geology, mineralogy and chemistry were collected for kaolinite-alunite association and bentonite occurring in the acid sulphate alteration environments. The samples from the borehols drilled during 1994-1995 have been used. Detailed geological survey of this territory followed the results, published previously by Forgáč (1972) and Čurlík et al. (1991).

Fluids, generated by an intrusion, located at depth, brought about extensive acid — sulphate wall rock alteration in the amphibolite-biotite andesite and derived clastic rock environments. Advanced alterations have been assigned to action of over heated steam, which affected apical art of the hydrothermal system within, or closely above the ground water table (Rye et al. 1992).

Substantially, the results confirmed the occurrence of 3 dominant mineralogical assemblages:

	I.	II.	III.
	alunite (30-50 %), quartz, tridymite, cristobalite, (20-30 %), kaolinite (10-30 %)	montmorillonite (40-50 %), quartz (20-30 %), pyrite (5-0 %), calcite (10 %)	montmorillonite (40-50 %), quartz (40-50 %)
SiO_2	35-40	51-55	59-63
Al_2O_3	20-30	15-17	18-20
Fe_2O_3	0.7-1.8	3-6	4-7
CaO	0.3-0.7	6-8	0.7-1.2
Na_2O	0.6-1.2	1-2	0.4-0.7
K_2O	1.5-3.5	1-2	1.9-2.2
SO_4^{2-}	15-25	-	-
S^{2-}	0.5-3.0	3-4	-
The thickness of the particular beds: I. (5-10 m — overburden of bentonite), II. and/or III. (10-20 m). Montmorillonite (III) exhibites beidelitic nature and suitability for the pillaring by Al-pillaring agents.			