CEC. Soils containing mica/smectites are characterized by almost complete dissolution of these pedogenic minerals which are characterized by low crystallinity and are extremely unstable under acid attack. The effect of treatments on the properties of vermiculitic soils was the dissolution of 2:1 silicates and carbonate, decrease of Vm degree of order and reduction of charge. The reaction of hydroxy-Al-vermiculite on the proton attack was the removal of interlayers and the appearance of expandable properties of Vm lattice.

PHENOMENON OF ILLITIZATION IN SOILS OF STEPPE AND FOREST-STEPPE ZONES

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An increase of illite content in fraction smaller than 1 μm from rock toward the upper horizons or illitization phenomenon is appropriate practically for all soils of steppe and forest-steppe zones. Arnaud and Mortland (1963) first discovered this phenomenon, in former USSR Chizhikova (1965) explored it. The results reported herein were obtained analyzing published data and our own investigations. The following hypothetical kinds of soil illitization can be distinguished: eluvial (relative accumulation of primary illite as a result of physical dispergation of micas, destruction and smectite loss); potassium-sorption (non-exchange absorption of potassium by smectite); re-crystallization (aggradation of smectite up to mica by fixation of potassium (Jackson, 1968)); and hydro-xerogenic (formation of illite-like structures by wetting and drying of soil). Except re-crystallization, all kinds of illitization are considered for the soils of steppe and forest-steppe zones. The most distinctly eluvial illitization is traced. In Moldova, eluvial illitization is displayed in consistent, statistically authenticated increase of illite-smectite parameters from young alluvial soils to more ancient chernozems of Quaternary terraces, to chernozems and forest soils on rocks of late-and early-Pliocene erosional surfaces. In the described order and as acid-alkaline properties of soils are shifting toward the acidic the of illite content in fraction less than 1 μm increases from 4 in alluvial to 16% in forest soils. This parameter decreases from loam to clay soils. The illite-smectite parameter of eluvial process intensity increases from 1 to 6 units from young to more mature soils (Alekseyev, 1999).

INFLUENCE OF POLYETHYLENE GLYCOL ON RHEOLOGICAL PROPERTIES OF NATURAL AND PEPTIZED BENTONITES

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The determination of rheological properties of bentonite-water systems is very important. It is necessary to know whether the system has a flocculated or deflocculated structure. There are several methods to know the interaction forces between particles and interaction behaviors. One of this methods is to determine the rheological properties. To observe the change of their flow properties, especially when various electrolyte, polymer and surfactants are added, is useful for describing them and determining their industrial uses. It is possible to provide this by the addition of the suitable additional substance in determined concentrations. The present work had two objectives: first, the determination of the fluidity of two types of bentonite-water systems, one prepared using a natural bentonite, and the other prepared from a peptized bentonite. Secondly, the development of a system with the desired fluidity by using polymers (two polyethylene glycohol polymers of different mole weights) of various concentrations. The influence of PEG-300 and PEG-8000 polymers on natural bentonite and Na-peptized bentonite (one decreases while another increases) is similar, however, the difference between thw degree of influence is also obvious.

SORPTION ABILITY AND ELECTROSURFACE PROPERTIES OF SAPONITE CLAY

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Saponite belongs to the three-octahedral type of smectites. The content of silica which depends on quantity of water may vary from 46% up to 56%, while the content of magnesia varies from 21% to 25%. Such substances as alumina, iron (III) oxide, sometimes chromium (III), nickel (II), iron (II) oxides and also calcium, sodium oxides are present due to isomorphism. Both saponite clays of the Khmelnitsky deposit were subjects of the investigation. The total ion exchange capacity of Tashkovsky saponite rock is (meq/g) 0.55, that of Varvarovsky saponite rock is 0.27, that of the pure mineral amounts to 0.70. Exchangeable ions are represented mostly by magnesium and small quantities of sodium, potassium, calcium, iron (III). The dependency of electrokinetic potential of saponite (ζ) on pH of medium was investigated by microelectrophoresis method. The electrokinetic potential of saponite is negative in a wide interval of pH - values. The saponite rock's ability to absorb radioactive strontium and caesium was studied in tracing experiment conditions in a static regime. The sorption effectiveness was found to be equal to 96.0% and 92.2% for caesium and strontium respectively. Qualitative and quantitative analyses were made to determine the presence of benzo-α-pyrene (BAP). The average content of BAP in the saponite rock is 61.2 10^{-10} kg/kg. Thus some valuable properties of saponite clay may give the reason to hope for an efficient usage of this mineral in processes of purification and deactivation of liquid products.

ELECTROOSMOSIS AND HYDROPHILICITY OF CLAY MINERALS

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Clay minerals, due to peculiarities of their crystallochemical nature, disperse spontaneously in polar liquids to particles of colloidal size. The high dispersity of clays is the reason of the dependency of the electroosmotic velocity P on the mass fraction of clay particles C. This dependency has the character of a curve with a maximum. The main features of the electroosmotic curve are: its left region indicates that a system is in a state of sol so that a free electrophoretic movement of particles takes place in the electric field; reversible transitions from sol to gel (and from the electrophoresis to the electroosmosis) are observed in the maximum of the curve; the right region corresponds to a structured system, which obeys the regularities of the electroosmosis. These regularities differ from the classical ones. The right region of the curve is described by the equation which permits to determine surface charge and thickness of boundary layer of water with peculiar properties. This equation can quantitatively characterize hydrophilicity of clay minerals. Values of "bonded" water, obtained by the proposed method of electroosmosis, decrease in the series: montmorillonite > aerosil > palygorskite > kaolinite. Thus the proposed method of the electroosmosis proves to be a reliable and available way of investigation of hydrophilic and other properties of clay minerals.

TRACING ELEMENT-TRANSFER PROCESSES AT THE EARTH'S SURFACE: INSIGHTS FROM THE SPECTROSCOPIC APPROACH

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Because of their finely divided nature and their high reactivity, the solid phases occuring at the Earth's surface play an important role in the dynamics of element transfer. Recent developments in spectroscopic methods provide detailed informations about actual structure of crystalline and/or amorphous solid phases. Our objective is to show that the nature of phases, the impurities and defects they contain, provide clues about conditions of formation and evolution of

materials at the Earth's surface. Several examples of tracing will be presented to illustrate this approach: (i) Radiation-induced defects were identified in kaolinite by Electron Paramagnetic Resonance (EPR), and used for the quantitative reconstruction of the past migration of radionuclides in the geosphere. This methodology is applied to natural analogues of radioactive waste repositories. (ii) The local structure of natural uranium-bearing Si, Al, Fe gels arising from oxidative weathering of a U-deposit was determined by Extended X-ray Absorption Fine Structure spectroscopy. This permits discussion of the mechanisms of U-trapping by these gels. (iii) An improved understanding of the different structural-Fe^{3+} species in kaolinite was achieved through modelisation of EPR data. Estimating populations of these impurities in kaolinites from vertical sequences brings constraints for modeling lateritic soil genesis (iv) The nature of phases and chemical distribution of Fe^{3+} in particulate and colloidal matter from a tropical catchment were determined by combining techniques such as EPR, FTIR and UV-visible diffuse reflectance spectroscopy. These results are used to discuss the origin and evolution of suspended matter in terms of erosion processes.

SHALE PROVENANCE IN THE SANTOS BASIN, SE BRAZIL

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Burial diagenesis had no perceptible control on the occurrence of clay minerals in the shales of the Santos Basin, where pelitic rocks composed of illite-smectite mixed-layers alternate with others containing pure smectite at depths greater than 3500 m. In these rocks, the distribution of clay minerals is largely controlled by regional stratigraphy and reflects mainly the composition of source rocks, the prevailing conditions of tectonism and paleoclimate during their weathering and the syn-depositional conditions in the basin. A study of trace elements and clay mineralogy reveals some characteristics of shale provenance during Early Cretaceous to Late Miocene times. From the Albian to Late Miocene, the shales were derived in the northern part of the Santos Basin from rocks of acid to intermediate compositions, typical of the Serra do Mar Mts. In the South, higher contents of Ni, Co and Cu indicate contribution of basalt detritus from the Parana Basin. This supply was intermittent From Late Santonian to Miocene times, due to tectonism in the source area and at the border of the Santos Basin. The rocks laid down during periods of tectonic activity, present lower contents of clay minerals with higher contents of chlorite and illite. The presence of pure smectite or chlorite-smectite mixed-layer is related to syn-depositional conditions. Higher contents of kaolinite were found in rocks younger than Eocene, following a period of relative tectonic stability.when the prevailing hot and humid climate could imprint its signature in the source areas.

THE CURVATURE OF SERPENTINES: HRTEM IMAGING AND ELASTIC MODELIZATION

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The curvature or tubular morphology of serpentines is generally explained by a structural mismatch related to the relative sizes of the tetrahedral and octahedral cations. For testing this assumption, $Ni_3(Si,Ge)_2O_5(OH)_4$ serpentine synthesis with progressive substitution for Si by the larger Ge ion, in tetrahedra, were studied by HRTEM-AEM. The results effectively show two structural morphologies directly related to the chemical composition: (i) curved structures ("roman tiles" or tubes), for Ge substitution rates lower than 25%; (ii) plane structures, for greater Ge rates. According to the theory of elastic thin plates, the curvature radius R of the plate is related to the difference between the surface stresses σ^+ and σ^- (on the two sides of the plate):

$$\frac{1}{R} = \frac{6(1-\nu)}{Eh^2}(\sigma^+ - \sigma^-)$$

where E is the Young's modulus, ν the Poisson's ratio, and h the thickness of the plate. In the case of a single serpentine layer, 0.7 -nm thick, the value $\sigma^+ - \sigma^- = 1$ J/m2 – considered as a reasonable example for Si-rich serpentines – would then produce a curvature with a radius R of about 17 nm. The preceding value belongs to the range R = 10 to 40 nm, observed in the "tiles" and tubes of the studied samples. It may be concluded that these "tiles" and tubes are probably formed by stacking of such elastically curved single serpentine layers. This process requires the creation of stacking defects, which make the whole crystal "rigid". For more Ge-rich serpentines, $\sigma^+ - \sigma^-$ probably vanishes, and the stacking of plane single layers leads to plane serpentine crystals.

AUTHIGENIC SMECTITE IN CRETACEOUS TURBIDITE SANDSTONES

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Turbiditic sandstones are the main petroleum reservoirs of Brazilian Passive Marginal Basins such as Campos, Sergipe and Esp'rito Santo. They are generally porous and partially cemented by calcite and kaolinite. The Maastrichtian Turbiditic Sandstones of Fazenda Alegre Field are important reservoirs of the emerse portion of Espírito Santo Basin. The sandstones are arkoses with 30% porosity containing biodegraded oil. However, differently than others, they present a high content of around 10% of authigenic clays. Smectite is the main diagenetic constituent which causes serious formation damage to the reservoirs in contact with unsuitable drilling fluids. Smectite with honeycomb texture occurs as pore filling and framework grain coating. Small content of pore filling kaolinite also occurs with vermicular habit of curved crystal aggregate sets. Kaolinites with similar features have been described as resulting from meteoric water influence. Paragenetic relationships show that smectite posdates kaolinite. These kaolinite was considered to be formed by meteoric water infiltration during telodiagenetic regime associated to a Cretaceous–Tertiary unconformity. Smectite is not only coating kaolinite but is also replacing it. A more detailed study including isotope and microprobe analysis and regional geological evaluation are being carried out in order to understand the sources of the smectite-precipitating fluids and the reasons for the drastic change in reservoir geochemical conditions.

AN APPLICATION OF CLAY ++ FOR THE QUANTITATIVE ANALYSIS OF MIXED-LAYERED CLAY MINERALS

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Clay mineral quantification by XRD is a complex process. The problems are greatest when there are mixed-layered clay minerals in the sample, particularly if the mixed-layered species are present in samples also including the simple clay types. The aim of this work is to illustrate a methodological sequence for qualitative and quantitative representation (QR) of complex clay samples. The methodological sequence proposed is as follows:

1 – Layer type determination using patterns obtained from Mg-saturated and glycerol solvated samples.

2 – Determination of mixed-layered proportion and order using patterns of EG-solvated samples.

3 – Simulation of the pattern of mixed-layered and simple clays using Mulcalc program. The simulated patterns obtained constitute a good XRD reference library but this is not a good method for obtaining a theoretical pattern for the studied sample, which must be manually composied.

4 – Interpretation of the pattern using Clay++ program for pattern matching to produce a QR. The absence of standards means that results obtained by Clay++ can not be checked for accuracy, but this method provides a good statistical value for the fit. The possibility to create a theoretical pattern to compare with the experimental one and to estimate the "goodness of fit" makes Clay++ a good tool to obtain QR results for samples containing several varieties of clays. In conclusion, the methodological sequence is a good tool to characterize qualitatively mixed layered and discrete clay mixtures and also gives a good quantitative representation of their composition.

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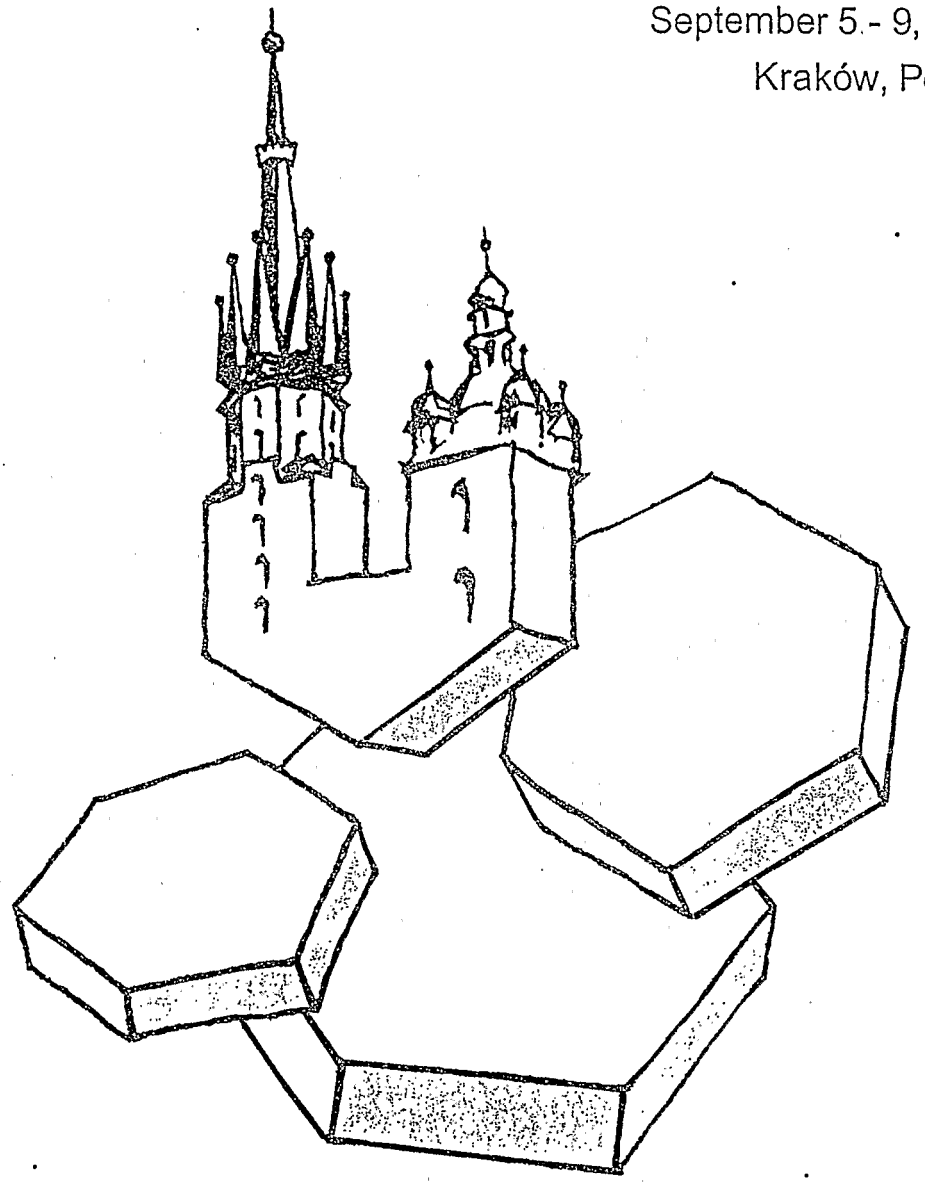

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