Third Mediterranean Clay Meeting

Jerusalem, Israel

September 30 – October 3, 2002

STATE OF ISRAEL

Ministry of Science,
Culture and Sport

The Hebrew University
of Jerusalem

CONTENTS

Third Mediterranean Clay Meeting
Jerusalem, Israel

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The conference will be devoted to the chemistry, physics, and geology of clay minerals and their applications in protecting the environment, in agriculture and in industry.

An important aspect of the Conference is to promote cooperation between scientists of Mediterranean countries. We hope that this Conference will also contribute to attempts of achieving peace and raising hopes in the region.

The Israel Ministry of Science, Culture and Sport is **a coorganizer** of the Meeting. The first scientific session of the Meeting, which deals with Environmental and Agricultural Applications of Clay-Minerals, is dedicated to the presentation of several achievements obtained throughout the three years of joint activities of several groups in Israel which collaborated in a large national project "Tashtiot". This project, funded by the Israel Ministry of Science, Culture and Sport proceeded during the period April 1, 1999 – July 31, 2002. The session also includes contributions by several guest speakers from Europe and Israel.

The Meeting is also sponsored by **The Hebrew University of Jerusalem** and additional contributions were obtained from: **The Israel Ministry of Agriculture, The Open University of Israel and The Peres Center for Peace.**

Location: Edmond J. Safra Campus (Givat Ram) of the Hebrew University of Jerusalem, Chemistry Building (Los-Angeles); Seminar Hall (Upper Ground Level).

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Program

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Monday, Sept. 30; 19.00 – 21.30
Reception at the Belgium House.

Tuesday, Oct. 1
Opening ceremony : 09.00 – 09.30
Greetings by representatives of: The Israel Ministry of Science, Culture and Sport; The Hebrew University of Jerusalem; Mr. Constantinos Papadimitriou, Economic and Commercial Counsellor, Embassy of Greece; and Organizers of the Meeting.

First Session – dedicated to the "Tashtiot" project of the Israel Ministry of Science, Culture and Sport.

Environment and Agriculture I. Applications of Clay-Minerals in the Design and Production of Environmentally Friendly Pesticide Formulations.

Chairman: Prof. Yoel Sasson

09.30: ***C. Forano***, *T. Alekseeva, Li Feng, J. Inacio, C. Taviot-Gueho & J.P. Besse (France)* : Interactions of Anionic Clays and Pesticides. 7

10.00: ***S. Nir***, *Y. Mishael (Israel), T. Undabeytia (Spain), G. Rytwo (Israel), B. Papahadjopoulos-Sternberg (U.S.A.), O. Rabinovitz, T. Polubesova & B. Rubin (Israel)* : Clay-Micelles as a System for Solving Environmental and Agricultural Problems. 8

10.25: Coffee break

10.50: ***Y. Mishael*** *(Israel), T. Undabeytia (Spain), O. Rabinovitz, B. Rubin & S. Nir (Israel)* : Slow Release Formulations of Anionic Herbicides incorporated in Micelles adsorbed on Montmorillonite. 9

11.15: ***Z. Gerstl***, *A.Nasser & U. Mingelgrin (Israel)* : Chitosan Clay Interactions. 10

11.40: ***T. Alekseeva***, *J. Inacio, C. Taviot-Gueho & C. Forano (France)* : Comparative Study of Atrazine Adsorption on Humic/Cationic and Anionic Clays Complexes. 11

12.05: ***Y. El-Nahhal*** *(Palestinian National Authority)* : Adsorptive Behavior of Terbutryn on Organoclay Complexes. 13

12.30-14.00: Lunch

Chairman: Dr. Zev Gerstl

14.15: ***G. Rytwo*** *(Israel)* : Testing the Gouy-Chapman-Stern Adsorption Model for Adsorption of Organic Cations to Soils. 14

14.40: ***M. Lado*** & *M. Ben-Hur (Israel)* : Soil Mineralogy Effects on Crust Micromorphology, Infiltration and Erosion. 15

15.05: ***O. Rabinovitz,*** *Y. Mishael, S. Nir, T. Polubesova, C. Serban & B. Rubin (Israel):* Testing the Release of Herbicides from Organo-Clay Formulations through a Thin Soil Layer in Funnels. 16

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15.30: Coffee break

Second Session - Posters

Chairperson: Prof. Lisa Heller-Kallai

15.50: Short oral presentations of posters followed by poster viewing:

Evening : Free: A visit to the Israel National Museum.

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Wednesday, Oct. 2

Third Session - Spectral and Colloidal Properties of Clays and Clay Minerals.

Chairman: Prof. Janos Kristóf

Chairman: Prof. Shmuel Yariv

Fourth Session - Nanoparticles

Chairman: Prof. Claude Forano

15.30 : Tour of Jerusalem followed by dinner. Sites visited included: 1. The Govenor's Palace; 2. The Old City: the market, the Holy Sepulchre, the Cardo, the Jewish Quarter; 3. Mount Scopus.

Thursday, Oct. 3

Fifth Session - Environment II. Applications of natural or modified clay-minerals in catalysis of reactions and recycling and treatment of water.

Chairman: Dr. Shlomo Shoval

Sixth Session - Geological aspects of clays and zeolites and their formation.

Chairman: Prof. Shmuel Yariv

Chairman: Prof. Arieh Singer

Seventh Session - Clay deposits and their applications : Ceramics and Archeology.

Chairman: Dr. Jiwchar Ganor

INTERACTIONS OF ANIONIC CLAYS AND PESTICIDES

C. Forano, T. Alekseeva, Li Feng, J. Inacio, C. Taviot-Gueho and J.P. Besse

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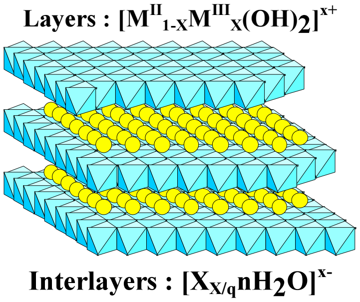

The Layered Doubles Hydroxides (LDH) display many similar or opposite properties compared with clay minerals in term of structure, ionic exchange properties, interaction with organic matter, rheology and catalytic activities. Their opened 2D structure is made by a stacking of positive $[M^{II}_{1-X}M^{III}_{X}(OH)_2]^{x+}$ extended layers separated by exchangeable anionic species $[X_{X/q}nH_2O]^{x-}$ (abbreviated as $[M^{II}$-M^{III}-$X]$. Their structure is considered as the anti-type phillo-silicate structure and this is the reason why they are often called anionic clays.

The use of LDH as adsorbents for pollutants and particularly for pesticides has been investigated now since many years following similar studies developed on clay minerals[1]. As anion exchangers, LDH are ones of the rare adsorbents specific for negatively charged pesticides but the hydrophilic surface of their layers combines to adsorb polar or protic molecules. As organoclays, LDH can be modified by intercalation of anionic surfactants. The hybrid materials then display hydrophobic van der Waals domains suitable for non polar organic molecule intercalation.

These synthetic minerals offer the possibility to tune the capacity and the nature of adsorption by changing the chemical composition of the host structure, the layer charge density, the surface charge, the exchangeable anion, the specific surface area.

Adsorption of MCPA, 2,4-D, 3,4,5-T, benzothiazuron, glyphosate, atrazine on [Mg-Al] and [Zn-Al] LDH and modified LDH has been studied. Adsorption isotherms arise from the contribution of both surface and internal adsorption which render the simulation with classical langmuir and Freundlich models rather limited. The intercalation of MCPA was followed using FTIR and XRD. Differentiation of outer mobile and inner immobile species has been evidenced for the first time by HR MAS NMR[2].

The influence of the chemical, structural and morphological properties of the adsorbents on the sorption capacity will be also presented.

1. L.M. Parker, N.B. Milestone, R.H. Newman, Ind. Eng. Chem. Res. **1995**, 34, 1196-1202
2. B. Combourieu, J. Inacio, A.M. Delort, C. Forano, Chem. Comm. **2001**, 2214.

CLAY-MICELLES AS A SYSTEM FOR SOLVING ENVIRONMENTAL AND AGRICULTURAL PROBLEMS

S. Nir[1*] *,Y.G. Mishael*[1]*, T. Undabeytia*[2]*, G. Rytwo*[3]*, B. Papahadjopoulos-Sternberg*[4]*,*
O. Rabinovitz[1]*,T. Polubesova*[1]*, and B. Rubin*[1]

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We describe the design and characterization of new nano-micro complexes which will be a basis for (i) slow release formulations of pesticides and (ii) efficient removal of organic anions from water.We developed slow release formulations of anionic herbicides, such as sulfometuron (SFM) whose leaching in soils is an environmental and economical problem. The herbicide was incorporated in positively charged micelles of quaternary amine cations, which in turn adsorbed on the negatively charged clay. Adsorption of octadecyltrimethylammonium (ODTMA) on montmorillonite was studied above and below the CMC (critical micelle concentration), i.e., 0.3 mM, respectively. The cation adsorbed at more than 200% of the cation exchange capacity of the clay at added concentrations above the CMC. An adsorption model indicated that above the CMC adsorbed micelles contributed significantly to the amounts adsorbed. The different nature of monomer and micelle adsorption was elucidated by using X-ray diffraction, freeze-fracture electron microscopy and dialysis bag measurements. SFM did not adsorb directly on the clay mineral and adsorbed on it at very low levels when the organic cation was added below its CMC. In contrast, SFM adsorbed at high levels on the clay mineral when incorporated in the micelles that adsorbed on the clay. The study (1) demonstrated the existence of an optimal ratio of ODTMA/Clay for maximal adsorption of SFM by the clay-micelle complex. Above this ratio the adsorbed fraction of ODTMA is reduced, whereas below this ratio micelles decompose into monomers and SFM is released to the solution. The new ODTMA-mont formulation yielded slow release of SFM in water. Analytical and bioassay tests in soil columns demonstrated significant reduction in SFM leaching when applied as a micelle-clay formulation in comparison to that of the commercial formulation. When SFM was applied in the new formulation at an amount 10-fold less than that of the commercial formulation, its herbicidal activity was more than twice that of the commercial formulation. Thus, the new formulation appears promising both from the environmental and economical points of view (2).

The micelle–clay system can be used to remove anionic pollutants from water. Preliminary results gave more than 99% removal of anionic herbicides, such as sulfosulfuron and sulfentrazone.

1.Y.G. Mishael, T. Undabeytia, G. Rytwo, B. Papahadjopoulos-Sternberg, B. Rubin and S. Nir. J Agric. Food Chem.*50 (2002) 2856.*

2. Y. G. Mishael, T. Undabeytia, O. Rabinovitz, B. Rubin and S. Nir. J Agric. Food Chem. *50 (2002) 2864.*

SLOW RELEASE FORMULATIONS OF ANIONIC HERBICIDES INCORPORATED IN MICELLES ADSORBED ON MONTMORILLONITE

Yael Golda Mishael[1], Tomas Undabeytia[2], Onn Rabinovitz[3], Baruch Rubin[3] and Shlomo Nir[1]

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The aim of this study was to design and test slow release formulation of sulfosulfuron (SFS), a sulfonylurea herbicide, whose leaching in soils is an environmental problem. SFS is negatively charged at moderately basic pH causing a severe problem of herbicide leaching to deep soil layers, migration to non-target areas and a reduction of the herbicidal efficacy (1, 2). In the proposed formulation the herbicide is incorporated in positively charged micelles of a quaternary amine cation, octadecyltrimethylammonium (ODTMA), which in turn adsorb on the negatively charged clay, montmorillonite.

Evidence for adsorption of ODTMA micelles on montmorillonite was provided by X-ray diffraction, freeze-fracture electron microscopy and dialysis bag measurements (3). SFS did not adsorb directly on the clay mineral, and adsorbed on it at low levels (1.1%), when the organic cation adsorbed on it as monomers. In contrast, a large fraction of SFS (98%) adsorbed on the clay when incorporated in micelles similarly to the trend found for another anionic herbicide, sulfometuron, (3).

Optimization of herbicide micelle clay ratios yielded high adsorption of SFS and low desorption. At 0.5-5% (w/w) formulation suspensions no SFS was detected in the supernatant, at times varying from hours to days. The herbicide concentrations measured in release experiments were at or under the HPLC limit of detection (0.5 ppm).

A plant bioassay showed that the micelle-clay formulation yielded 2-fold shoot growth inhibition at the top 4 cm of the soil in comparison with the commercial soluble granular formulation (Monitor, 75% ai). At a depth of 16-20 cm the commercial formulation yielded 71% shoot growth inhibition indicating a high degree of herbicide leaching, whereas the micelle-clay formulation yielded half of that value i.e., a reduction in leaching when applying the micelle-clay formulation. These characteristics make the new formulation promising from the environmental and economical points of view.

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(2) I. D. Black, R.N. Pederson, A. Flynn, M. Moerkerk, C. B. Dyson, R. Kookana, N. Wilhelm. Aust. J. Exp. Agric. *39*, 465 (1999).
(3) Y.G. Mishael, T. Undabeytia, G. Rytwo, B. Papahadjopoulos-Sternberg, B. Rubin and S. Nir. J Agric. Food Chem. 2002a. (in press).
(4) Y. G. Mishael, T. Undabeytia, O. Rabinovitz, B. Rubin and S. Nir. J Agric. Food Chem. 2002b (in press).

CHITOSAN CLAY INTERACTIONS

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Chitosan is a partially acetylated glucosamine biopolymer produced from the deaceylation of chitin. Chitosan is hydrophobic and a known sorbent for heavy metal ions because of the amino (-NH_2) and/or hydroxy (-OH) groups on the chitosan chain can act as coordination sites. Some work has also been carried out on the sorption of dyes by chitosan.

In the present study the interaction of chitosan and montmorillonite was studied as a function of pH. Sorption isotherms of chitosan on montmorillonite were obtained at pH 4.6 and 6.0 in buffered solutions. The use of clay-chitosan complexes for removal of ionic and nonionic pollutants from aqueous solutions was determined. The heavy metals studied include Zn, Ni and Cd. The organic contaminants studied are atrazine (solubility 35 mg/L), alachlor (solubility 200 mg/L) and bromacil (solubility 800 mg/L). Sorption isotherms on clay-chitosan complexes will be determined (using unaltered clay as a reference).

COMPARATIVE STUDY OF ATRAZINE ADSORPTION ON HUMIC/CATIONIC AND ANIONIC CLAY COMPLEXES

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Most pesticides being hydrophobic they have a high affinity to organic molecules (e.g. humic acid) because of the possibility for non-polar, so-called, hydrophobic and charge transfer interactions additionally to ion exchange, ligand exchange, hydrogen bondings and van der Waals interactions which are provided by clay surfaces (1). Atrazine (AT), widely used in agriculture, is an hydrophobic neutral (weak basic) pesticide. Natural clays as well as hydrotalcites (LDHs) being generally hydrofillic are not good sorbents towards such hydrophobic molecules. Modification of clay surfaces from hydrofillic to hydrophobic with organic polymers such as humic acids (HA) makes them organofillic and thus able to participate in hydrophobic bonding.

The aim of the present work was the investigation of AT adsorption by cationic clay/HA and anionic clay/HA complexes. Cationic clay was Ca-form of industrial Aldrich Bentonite without additional purification. Anionic clay (synthetic hydrotalcite) used for experiments was $Mg_2Al(OH)_6NO_3 * H_2O$ ($LDHNO_3$) synthesized by coprecipitation method. HA was Aldrich Na-salt. Batch equilibration study for 24 hours at 25°C with 5-400mg/l HA solutions and 50mg/50ml solid/liquid ratio was undertaken. UV spectrophotometry was used to determine HA concentrations. The sorption isotherms were nonlinear in both cases. $LDHNO_3$ has the higher affinity to HA than Ca-bentonite giving the H-type adsorption isotherm with 87% mean adsorption and maximum adsorption capacity of 230 mg/g compared to 13% and 34mg/g respectively for Ca-bentonite. HA increased visibly specific surface areas of both clays by increasing their mesoporosity. FTIR and XRD spectra of clay/HA complexes testify the surface adsorption of HA on LDH which provides positive surface charge. Observed hydrolisis of LDH with formation of $Al(OH)_3$ could also create adsorption centers for HA. At pH of experiment (7-8) repulsion of HA molecules with bentonite layers would rather occur. FTIR spectra show the traces of hydrophobic interactions.

For AT adsorption $LDHNO_3$ and its complexes with 2 and 10% HA, Ca-bentonite and its complex with 10% HA were prepared basing on the results of above experiments. Batch equilibration study at 25°C for 24 hours with 3-30 mg/l AT solutions and 1g/10ml solid/liquid ratio was undertaken. HPLC measurements of solutions after microfiltration with “Oasis” cartridges was used to determine the AT concentration. No AT adsorption on $LDHNO_3$ took place which confirm that hydrotalcites are not good sorbents for hydrophobic pesticides (2). For all other cases adsorption isotherms fitted the Freundlich equation - x/m=KfC1/n. The adsorption capacity (Kf) values were 0.82-45.5 (mg*g-1)/(mg*l-1) being the smallest for LDH with 2% HA and highest for Ca-bentonite with 10% HA. The mean amounts of AT adsorbed were 19% for LDH+2%HA, 42% for LDH+10%HA, 29% for Ca-bentonite and 78% for Ca-bentonite +10% HA. These data indicate that HA was the main factor controlling AT adsorption and support the previous studies (3,4). FTIR spectra suggest the occurance of multiple binding mechanisms between clay complexes and AT due to the coexistance of heterogeneous adsorption sites.

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ADSORPTIVE BEHAVIOR OF TERBUTRYN ON ORGANOCLAY COMPLEXES

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This study aimed to investigate the adsorption behavior of terbutryn on montmorillonite exchanged by quaternary ammonium or quaternary phosphonium organic cations from distilled and hyper saline water. Equilibrium concentration of terbutryn was determined by HPLC. The adsorbed amounts of terbutryn from distilled water on montmorillonite exchanged by tetraphenylphosphonium (TPP) at a loading of 0.5 mmol/g clay were the highest among all cases. Adsorption of terbutryn on clay saturated with quaternary phosphonium cations was higher than adsorption on clay saturated with quaternary ammonium one. An interesting outcome of the study is that addition of NaCl dramatically increased the adsorbed amounts of terbutryn in all test organoclay complexes. The changes in the free enthalpy of the adsorption reaction provide an evidence of physical adsorption and indicate that the reactions are spontaneous. These findings provide better understanding of the behavior of terbutryn on different organoclay complexes, and can be useful for further development of ecologically acceptable formulations to minimize the risk to groundwater, and to reduce the applied rates.

TESTING THE GOUY-CHAPMAN-STERN ADSORPTION MODEL FOR ADSORTPION OF ORGANIC CATIONS TO SOILS

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An effective adsorption model was developed in 1978 by S. Nir[1] for predicting adsorption to synthetic membranes, and adapted by him afterwards to clay minerals[2]. The main principles of the model are the solution of the electrostatic Gouy-Chapman equations, while calculating adsorbed amounts of the cations as the sum of those residing in the double-layer region, and the cations chemically bound, in a closed system. Thus the equilibrium concentration in solution is influenced by the adsorption, as a function of the amounts bound. During the years the model was developed and adapted to several systems (see review[3] and latest adaptation for binding to two different types of sites on the same clay mineral[4,5]), and in most cases the fit between measured and calculated results was very good, after calibrating the model for the chemical tested, with only two adjustable parameters for each chemical. After the calibration the model could predict without any further adaptation the amounts adsorbed for a very wide range of conditions, such as changes of three orders of magnitude in the ionic strength, or in the presence of several competing mono- di- and trivalent ions at different concentrations of each.

In the current work we tested the applicability of the mentioned model for the adsorption of a monovalent and a divalent organic cation to three different soils, considering the amount of clay, the cation exchange capacity and the specific surface area of the soils.

References

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SOIL MINERALOGY EFFECTS ON CRUST MICROMORPHOLOGY, INFILTRATION, AND EROSION

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Soil mineralogy has substantial effects on aggregate stability and, therefore, may influence infiltration rate (IR) and soil loss under rainfall. The objective was to study the effects of soil mineralogy on crust micromorphology, infiltration and erosion. Five soils with differing properties were subjected to 80 mm of simulated rainfall. The aggregate stability of these soils was determined by the fast wetting method. The mean-weight diameters of the particles after the fast wetting were 2.8 mm in a clayey, kaolinitic soil, 0.25 and 0.31 mm in clayey and sandy loam, montmorillonitic soils, respectively, and 0.84 and 0.87 mm in clayey, non-phyllosilicate soils. The final IR was 20.5 mm h^{-1} in the clayey, kaolinitic soil and $\leq$ 9.3 mm h^{-1} in the remaining soils. Scanning electron microscope observations indicated that the kaolinitic soil had a thin crust (~ 0.1 mm) containing large particles (~ 0.1 mm), whereas the montmorillonitic soils had thicker crusts (> 0.2 mm) comprising either small (~ 0.02 mm) particles with a very developed washed-in zone underneath or large (~ 0.2 mm) ones with fine material between them. The crust layer in the non-phyllosilicate soils was ~ 0.2 mm thick and composed of fine particles ~ 0.01 mm. The high aggregate stability and the low dispersivity of the kaolinitic soil, which minimized soil detachment, and its low runoff, which minimized its transport capacity, limited the soil loss to 0.33 kg m^{-2}, whereas the low aggregate stability and high runoff of the montmorillonitic soils contributed to their soil losses of 1.24 and 1.14 kg m^{-2}. The intermediate aggregate stability and the high runoff of the non-phyllosilicate soils accounted for their intermediate soil losses of 0.75 and 0.8 kg m^{-2}.

TESTING THE RELEASE OF HERBICIDES FROM ORGANO-CLAY FORMULATIONS THROUGH A THIN SOIL LAYER IN FUNNELS

Onn Rabinovitz [1], Yael Mishael [2], Shlomo Nir [2], Carina Serban[2], Baruch Rubin[1].

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Organo - clay formulations of herbicides can reduce the leaching and movement of active ingredient from application sites to non-target points, such as open water reservoirs, streams, ground water sources, and neighboring fields. Development of a new formulation is a lengthy and expensive process, primarily because it involves testing in the field. The objective of this work is to estimate the release of the herbicide from the organo-clay formulation under irrigation conditions by a "funnel experiment". The herbicide formulation was applied on a very thin soil layer deposited on filter paper inside a Buchner funnel (10 cm diameter), and irrigated with 50 mm of water. Ten fractions of the irrigated water solution were collected. The leached herbicide concentration was determined analytically by HPLC or GC, and by a bioassay. In the case of sulfosulfuron all the active ingredient was released from its commercial formulation after the 10th wash, whereas only 4% was released from the new herbicide organo- clay formulation of the herbicide. The new organo-clay formulation of sulfentrazone released after the first wash only 0.49% of the initial amount, and about 3% after the 6th wash. The commercial formulation released 85% of its initial amount and after the 6th wash the entire active ingredient was released. We considered that the rate of release followed first order kinetics, but it should be recalled that the process is dynamic and re-adsorption may occur. If A is the initial adsorbed amount of herbicide (sulfosulfuron), and P is the fraction which remains adsorbed following each washing, the remaining amount of herbicide adsorbed after the first wash is AP, and the amount of herbicide released is A(1-P). After n washes the remaining amount is AP^n and the amount released at this washing is $AP^{n-1}(1-P)$. For formulations of the herbicides sulfometuron and sulfentrazone we defined a parameter α as the deviation of the released fraction from the above equation, such that $A(1-q)(1-q\alpha)$ is amount of the herbicide adsorbed after the second wash and $A(1-q)q\alpha$ is the amount of herbicide released after the second wash. Evaluation of α gave good fit between the predicted and observed concentrations of the herbicide in the water solution. By utilizing the results of funnel experiments with derived experimental parameters, and expressions of the disperssion-convective flow of an inert solute in soil columns, we will able to estimate the distribution of the free herbicide at different soil depths and at given times in soil columns. We intend to verify the release and transport of the active ingredient by using ^{14}C-sulfosulfuron. The funnel experiments will enable to improve the new organo-clay formulations before testing them under field conditions.

THERMO-XRD INVESTIGATION OF MONTMORILLONITE MECHANOCHEMICALLY TREATED WITH UREA

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Monoionic Wyoming Me-Montmorillonte (Me=H, Li, Na, K, Rb, Cs, NH_4, Ca, Mg, Sr, Ba, Cu, Co, Fe, Mn and Al) were dry ground with urea in the ratio M:U=1:2; 1:1; 1:0.5 and 1:0.25. Mechanochemically treated samples were analyzed by X-Ray powder method at room temperature and after gradually heating at 150, 175, 200, 225, 325 and 375 ^{o}C for 3h during each temperature in air atmosphere.

The samples with ratio Mont:U=1:2; 1:1 and 1:0.5 show the presence excess of urea in addition to the peaks of the interlayer complex. After heating at the highest temperature the Me-Montmorillonite/urea show the following d(001) spacing (Å):

X	**H**	**Li**	**Na**	**K**	**Rb**	**Cs**	**NH_4**	**Ca**
d	**11.1**	**10.3**	**10.1**	**10.3**	**11.8**	**11.9**	**10.4**	**12.6**
	Mg	**Sr**	**Ba**	*Cu*	**Co**	**Fe**	**Mn**	**Al**
	11.3	**12.6**	**12.1**	**10.3**	**10.3**	**11.1**	**10.3**	**12.5**

Diffractograms of samples after grinding in ratio Mont:U=1:0.25 did not show any of the characteristic peaks of urea but that of the interlayer spacings appeared with the same spacing observed with the ratio 1:2.

The results of the Thermo-XRD analysis demonstrated that the mechanochemically treatment is effective method to obtain the intercalation complexes of smectite with some non-charged molecules.

THERMAL INTERACTIONS OF KAOLINITE WITH POTASSIUM CARBONATE REVISITED

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Previous studies established that kaolinite reacts with K_2CO_3 on dehydroxylation and that the transformations leading up to the high temperature polymorphs of $KSiAlO_4$ are topotactic. In recent years there has been considerable interest in reactions of kaolinite and metakaolinite with alkalis to produce zeolites as well as in the phases obtained at higher temperatures.

In the present study we compared the products of solid state reactions obtained with different kaolinites on heating with K_2CO_3 under various conditions. After dehydroxylation metakaolinite was not formed, but a different X-ray amorphous phase developed instead, with an infra-red spectrum resembling that observed in the synthesis of zeolites on the one hand and in the transition from zeolites to high temperature phases on the other. The absorptions can be assigned to interconnected AlO_4 and SiO_4 tetrahedra.

The first polymorph of $KSiAlO_4$ that crystallized in these reactions was synthetic kaliophilite. It was obtained under significantly milder conditions than by any other method of synthesis reported in the literature.

The reactions of different kaolinites with K_2CO_3 were similar in trend, but differed in detail.

WIEN EFFECT MEASUREMENTS IN DILUTE SUSPENSIONS OF CHARGED CLAY PARTICLES

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ABSTRACT

Deviation from Ohm's law in the form of the electrical conductivity (σ) increasing with the applied electrical field strength (E) is known as the Wien effect. With the help of a home made, low-cost apparatus yielding a short (~ 10^{-6}s) DC pulse that enables electrical fields of up to 2 x10^7 V/m, we have measured the increase in σ of mono- and divalent cationic electrolyte solutions and suspensions made of pure clay minerals and from the clay fraction (<2μm) separated from natural soils. The increase in the electrical conductivity of the clay suspensions with increasing E was up to two-fold. This general trend of increase can be explained by a greater dissociation of the counter ions from the particles, thus increasing the contribution of these ions to the overall σ of the suspension. In this sense the variation of σ with E reflects the "bonding strength" of the counter ions to the charged particles. Other possible mechanisms contributing to the measured increasing $\sigma(E)$ functions are the rotation of the platy clay particles and their alignment with the applied electrical field and the slipping plane encroaching on the particle surface. In this lecture we want to present the short high-voltage pulse apparatus we developed and results of Wien effect experiments with homocationic montmorillonite suspensions of different exchangeable cations, ionic strengths and particle concentrations.

CONTROLLED-RATE THERMAL ANALYSIS OF KAOLINITE AND THEIR INTERCALATES

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The industrial application of kaolinite, an important industrial raw material, is closely related to its surface reactivity. The reactivity of kaolinite internal surfaces can be tested by intercalation, i.e. via the insertion of low molecular weight organic compounds (potassium-acetate, formamide, hydrazine, etc.) between the kaolinite layers consisting of the two-dimensional arrangements of tetrahedral (siloxane) and octahedral (gibbsitic) sheets [1,2].

Thermal analysis is one of the major instrumental analytical techniques most suitable for the qualitative and quantitative investigation as well as for the structure elucidation of organo-clay complexes. Simultaneous TG-DTG-DTA studies of intercalated kaolinites give lots of information on the composition, thermal stability and structure of kaolinites intercalated with potassium acetate, cesium acetate, urea, formamide, dimethyl sulphhoxide and hydrazine [3,4].

A detailed investigation of the various intercalates, however, require a good resolution - much higher than that an experiment can ever offer under dynamic heating conditions- in order to reveal the fine structure of these complexes. Controlled-rate thermogravimetric analysis (CRTA) capable of performing thermal decomposition reactions at a slow, pre-set rate is the method of choice. With this technique time enough is provided for the inherently slow transport of heat between the furnace chamber and the sample and for the establishment of an equilibrium between gas-phase diffusion processes of opposite direction transporting de-composition products from the sample to the furnace chamber and furnace gas to the sample to replace gas-phase decomposition products. With this technique a complete separation -and quantitative determination- of surface-bonded (adsorbed) and strongly-bonded (intercalated) formamide could be attained [5]. For hydrazine-intercalated kaolinites three different types of bonded hydrazine could be identified [6]. The CRTA method can also be used for the study of various kaolinites mechanochemically activated prior to intercalation. The bonding strength of the reagent as well as the change of the number of the active surface sites as a function of activation time can be quantitatively evaluated.

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VISIBLE – SPECTROSCOPY STUDY OF THE ADSORPTION OF ALIZARINATE BY AL – MONTMORILLONITE IN AQUEOUS SUSPENSIONS AND IN SOLID STATE

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Abstract

The adsorption of the monovalent anionic dye alizarinate onto Na- and Al-montmorillonite was carried out by adding the dye into aqueous clay suspensions. Electronic spectra of aqueous suspensions and of dry dye-clay complexes were studied. Na-montmorillonite adsorbed only a part of the added dye. With total amount of alizarinate up to 5 mmol dye per 100 g clay the adsorption of the dye takes place on the broken-bonds leading to peptization of the clay. Al-montmorillonite adsorbed alizarinate completely up to 10 mmol per 100 g clay. From this loading there was a partition of the dye between the clay and the supernatant. The maximum adsorption for Na- and Al- clay was 4 and 25 mmol dye per 100 g clay respectively. Absorption bands in the spectrum of Al-montmorillonite suspensions (488-504 nm) appear in longer wavelengths than in the spectrum of dried Al-montmorillonite (415-455 nm). Thermo-X-ray study of these clay-alizarinate complexes suggests that the organic compound was located in the interlayer space in Al-montmorillonite but was not located there in Na-montmorillonite. In Al-montmorillonite alizarinate formed a coordination complex with exchangeable Al^{3+}. In Na-montmorillonite it formed bonds with Al exposed on the broken-bonds sites.

VARIABILITY IN WATER SORPTION AND IN PARTICLE THICKNESS OF STANDARD SMECTITES

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Variability in sorbed water content was studied on several standard smectites, as dependent on the relative humidity (**RH** = 0.5; 0.95 and 1.0), on temperature (constant 30° C, and variable room temperature) and on sorption time (**ts** = 1, 12 and 32 days). Therefrom the specific surface, **S** and particle thickness, **δ** were estimated, as proportional and inversely proportional to the sorbed water content, respectively. Generally **δ** decreased with the increase in the factors mentioned above and this effect was analyzed.

The thickest particles in dry state were found in hectorite and in synthetic Mica/Smectite (SHCa-1 and Syn-1, **δ** = 22 and 20 unit layers, u.l., respectively), the thinnest ones - in Ca-smectite (SAz-1) and in nontronite (SWa-1, **δ** = 5 to 6 u.l.) and the intermediate both in Na-smectite (SWy-1) and in Ca-smectite (STx-1), **δ** = 12 and 8 u.l., respectively.

These values were not constant: on prolonged storage at **RH** = 1.0, **ts** = 32 days, the smectite particles disintegrated gradually into separate cystallites, **δ** = 3 to 5 u.l. thus close to the thickness measured by **XRD**. An exception was hectorite, SHCa-1, with **δ** = 6 to 8 u.l. possibly due to „glueing" by calcium carbonate present.

In the clay-water system **δ** is close to that measured at **RH** = 0.95, i.e. 5-7 u.l., except SHCa-1 with **δ** = 9-10 u.l.

The decrease in **δ** (delamination) observed on increasing **RH**, was partly reversible. The hysteresis between water sorption on its increasing (**WS**) and water retention on its lowering to **RH** = 0.5 (**WR**) was especially pronounced in SHCa-1, SWy-1 and Syn-1 of initially thick particles. This was due either to a different number of the sorbed water layers, higher in **WR** (three-molecular in **WR**, bi-molecular in **WS**), or to incomplete collapse in **WR**.

Table 2. Average particle thickness, **δ** [u.l.], estimated from sorbed water content at 30°C,

Test	**RH**	SHCa-1	SAz-1	SWy-1	Syn-1	STx-1	SWa-1
a	b	c	d	e	f	g	h
bi-molecular	0.5	21.8	5.4	12.0	19.7	7.7	5.8
WS three-molec	0.95	9.7	4.8	6.8	6.8	5.8	5.3
three-molec	1.0	**7.8**	**4.4**	**5.5**	**3.8**	**3.9**	**4.0**
XRD* nm	ethylene	6.6	6.2	8.1	-	8.0	6.6
u.l.	glycol	**4.0**	**3.7**	**4.9**		**4.8**	**3.4**
three-molec	1.0	**6.9**	**4.3**	**5.0**	**4.4**	**4.7**	**3.9**
WR three-molec	0.95	9.3	4.6	6.0	5.7	5.4	4.9
bi-molecular	0.5	15.2	5.2	9.2	14.4	7.1	5.4
three-molec	0.5	22.8		13.8	21.4		

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SMECTITE NANOFILMS

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The tiling of elementary smectite platelets and the organization of molecules at the surface can be realized with the Langmuir-Blodgett (LB) technique. The method is based on the selective ion exchange reaction between the elementary smectite particles in a dilute aqueous suspension and amphiphilic cations at the air-water interface of the suspension in a LB trough. Films consisting of a monolayer of clay particles with the amphiphilic cations loaded on one side of the clay particles are deposited on a glass substrate either by vertical or horizontal deposition. Atomic force microscopy is used to reveal the ordering of the elementary clay particles. When the films are deposited at low or zero surface pressure, layers with submonolayer coverage of clay particles are obtained. When the surface pressure in the LB trough is increased, a continuous layer of clay particles is deposited. The organization of the adsorbed molecules is studied by vibrational spectroscopy, UV-Vis and fluorescence spectroscopies. With noncentrosymmetric dyes nanofilms with nonlinear optical properties are obtained. When two dyes such as oxacarbocyanine and rhodamine B are used energy transfer from oxacarbocyanine to rhodamine B is realized in the film.

Amphiphilic alkylammonium cations have a two-dimensional crystalline structure at the surface, pointing towards a close-packing. The alkylchains of the dye molecules are more or less randomly oriented in the films. This points to the absence of close-packing.

SEMICONDUCTOR NANOCRYSTAL QUANTUM DOTS AND QUANTUM RODS: FROM BASIC SCIENCE TO APPLICATIONS

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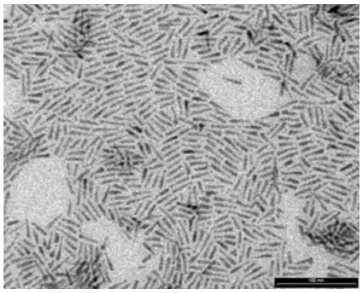
Semiconductor nanocrystals have unique size dependent optical properties governed by the quantum confinement effect. Spanning a diameter range of 2 to 20 nm, they serve as a model system for the evolution of properties from the molecular regime to the solid state, and are also potential building blocks of devices in nanotechnology. Furthermore, modifications of the colloidal synthesis conditions provide shape control allowing for the preparation of rod shaped particles, quantum rods, that manifest the transition from a zero dimensional quantum dot, to a one dimensional quantum wire.

In this talk we will introduce this field based on results obtained in our laboratory. The colloidal synthesis of high quality semiconductor nanocrystals and quantum rods of CdSe and InAs will be described. The size dependence of the electronic level structure reflecting the 'artificial atom' properties of these artificial structures will also be presented, where we use both optical and tunneling spectroscopy method to study these properties. Finally, two types of optical devices based on these nanocrystals will be presented. The first example is the incorporation of nanocrystals within a semiconducting polymer providing a first demonstration of an efficient, 'plastic based' light emitting diode covering the near infra-red telecommunication range will be reported. The second example is the observation of lasing from quantum dots and quantum rods in a cyl



TEM of CdSe quantum rods, with average size 25*4 nm.

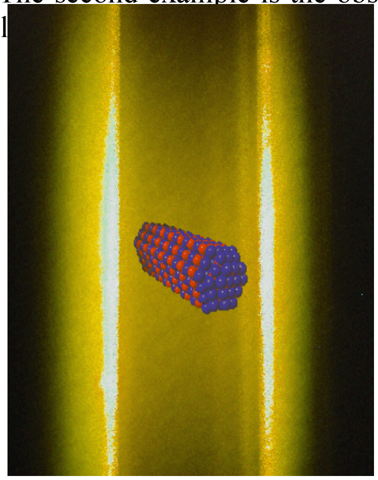


Photo of polarized lasing from a cylindrical microcavity loaded with CdSe semiconductor quantum rods. An illustrative model for the rod is presented in the center

BIFUNCTIONAL ORGANO-CLAYS FOR DETOXIFICATION OF INDUSTRIAL WASTEWATER

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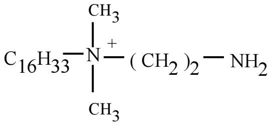
Organoclays are powerful sorbents for nonionic organic pollutants. They are, therefore, often used to remove toxic compounds from industrial wastewater. However, by adsorbing such compounds from wastewater onto organoclay, we merely change one environmental problem for another because the undesirable material accumulates on the organoclay. To overcome this problem we have developed a novel organoclay which not only sorbs toxic organic compounds, but also catalyzes their decomposition or hydrolysis. Such organoclays, termed bifunctional organoclays, are based on quaternary ammonium cations that contain a second functional group that is able to catalyze the desired reaction. To demonstrate this we present here a bifunctional organoclay with the cation N-hexadecyl-N,N-dimethyl-N-3-aminoethyl quaternary ammonium (**I**)



$$C_{16}H_{33}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{N}}}-(CH_2)_2-NH_2$$

I

To demonstrate the catalytic effect of this organoclay (I) on the hydrolysis of methylparathion (MP), distilled water was spiked with 10 mg/L MP and the release of p-nitrophenol into solution was determined. The hydrolysis of MP in the presence of the bifunctional organoclay (I) is presented in Fig. 1 in comparison with its spontaneous hydrolysis and its hydrolysis in presence of a natural bentonite clay, an organoclay with dodecyltrimethyl ammonium cation (DTMA), and the cation monomer (I) in solution.

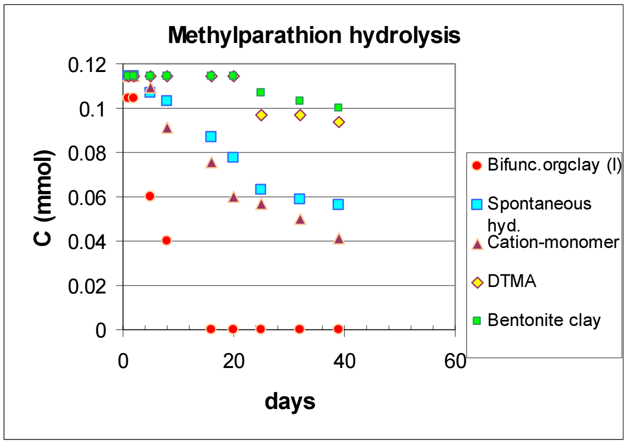


Figure 1. Hydrolysis of MP by organoclay (I) and several controls

The catalytic effect of organoclay I can be attributed to the free amino group on cation **I** that acts either via a nucleophilic attack or a general-base catalysis.

A NEW APPROACH TO UNDERSTANDING ORGANIC COMPOUND INTERACTIONS WITH ENVIRONMENTAL SORBENTS: I. THEORY AND APPLICATION TO MINERAL AND NATURAL CLAY SORBENTS

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Linear free energy relationships (LFERs) based on distribution coefficients between the aqueous phase and the sorbent are often unsuccessful for interpreting sorption mechanisms in environmentally important sorbents because they comprise contributions not only from solute interactions with the sorbent, but also from hydration of the solute in bulk water. To avoid this problem, we suggest an approach for studying interactions between organic sorbates and environmentally important sorbents using a thermodynamic cycle to eliminate interactions between the solute and bulk water. In this approach, aqueous distribution coefficients are converted to gas phase distribution coefficients that are related to the free energy of transfer from the gas phase to the hydrated sorbent, and include contributions from all interactions occurring during the transfer. Gas phase distribution coefficients are compared for different compounds with similar molar refraction values to give insights into the nature of specific and non-specific interactions of organic molecules with environmental sorbents. This approach can be used for any environmentally important sorbent, including organic matter, oxide mineral surfaces, and clay minerals (ref. 1,2).

We specifically illustrate the thermodynamic cycle approach for sorption of organic molecules at oxide mineral surfaces. In particular, we explore the concept of organic compound partitioning into a hypothetical vicinal water domain adsorbed at mineral surfaces by examining the solvating ability of vicinal water as compared with bulk water and organic solvents. Because water has stronger interaction energies with mineral surfaces than HOCs, mineral surfaces are coated with at least one layer of strongly sorbed water. It was suggested that this strongly sorbed water layer prevents HOCs from interacting directly with mineral surfaces. A layer of structurally-oriented water, termed vicinal water, was hypothesized to extend outward from this strongly sorbed layer, and HOC interactions with mineral surfaces were suggested to be via partitioning directly into this vicinal water.

Based on our anaylsis using the thermodynamic cycle, we conclude that the hypothetical vicinal water sorption domain at mineral surfaces would have the following attributes: (i) a size sensitivity for organic molecule distribution coefficients similar to organic media; (ii) a strongly suppressed ability to dissolve organic compounds as compared with organic media; (iii) a similar solvating ability as bulk water for small molecules and a tendency to exceed the solvating ability of bulk water for larger molecules; and (iv) negative entropy changes upon partitioning of organic compounds between bulk water and vicinal water, implying a stronger ordering effect than bulk water. Conclusions (i) and (iv) are apparently contradictory, which casts doubt on the validity of the "vicinal water as partitioning domain at mineral surfaces" hypothesis.

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A NEW APPROACH TO UNDERSTANDING ORGANIC COMPOUND INTERACTIONS WITH ENVIRONMENTAL SORBENTS. II. SORPTION TO ORGANOCLAYS

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Clay minerals in which the inorganic cation is replaced with an organic cation are well known to strongly sorb different organic compounds from aqueous solutions. Based on the high sorption efficacy of organoclays, different engineering, environmental and agricultural organoclay applications were proposed, e.g. slurry walls, landfill clay liners, waste water and contaminated ground water treatment, preparation of slow release formulations of herbicides, etc. Design of the organoclay applications needs detailed information on mechanisms of organic compound sorption interactions, including the effects of sorbate structure and the nature of the exchanged organic cation. Traditional analysis of aqueous sorption isotherms of organic compounds may be significantly complicated by the presence of water. Hydration affects both organic compound state in the bulk water phase and the sorbent phase, possibly masking molecular interaction forces occurring between sorbate molecules and the sorbent. Hence, using aqueous sorption isotherms to evaluate the role of many important processes such as specific interactions between the hydrated organoclay sorbent and sorbate, sorbate/water competition, organic sorbate-sorbed water interactions, etc. may become very complex.

In part, this problem may be overcome by converting aqueous sorption isotherms (or distribution coefficients) to the transfer of the compound from the gas phase or from an inert hydrocarbon solvent to the completely hydrated sorbent. This methodology excludes solute-water interactions and provides a real measure for the intensity of sorbate interactions in the sorbent phase. The methodology proposed earlier for natural environmental sorbents (refs 1-3) is applied now for organic compound sorption by organoclays. Analysis of sorption interactions in organoclays, at a certain selected sorption uptake level, is carried out on the basis of Eq. (1):

$$\text{Organoclay efficacy}= \log K_d + \log H_{C_{16}H_{34}} - \log H_w - \log \frac{OC}{OC_{C_{16}H_{34}} d_{C_{16}H_{34}}} \qquad (1)$$

where K_d is the experimental aqueous distribution coefficient, $H_{C_{16}H_{34}}$ and H_w are organic compound Henry coefficients in *n*-hexadecane and water, OC and $OC_{C_{16}H_{34}}$ are organic carbon contents of the organoclay sorbent and *n*-hexadecane, and $d_{C_{16}H_{34}}$ is *n*-hexadecane density. The first three terms on the right side of the Eq. (1) convert K_d into the distribution coefficient between the *n*-hexadecane phase and the hydrated organoclay sorbent. The conversion is purely thermodynamic cycle-based procedure and does not affect the nature of the interactions in the sorbent phase. The fourth term on the right side of the Eq. (1) is the distribution coefficient expected when all the organoclay carbon would behave as *n*-hexadecane. As such, the Eq. (1) demonstrates the efficacy of the organoclay as compared with a pure *n*-hexadecane phase. Based on this approach, efficacy of organic (aliphatic and aromatic) clay coating for aqueous sorption of different (polar and non-polar) organic compounds and potential sorption mechanisms will be discussed.

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REMOVAL OF POLLUTANTS FROM WATER USING OPTIMIZED MICELLE-CLAY SYSTEM

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The use of surfactants in the form of micelles for design of herbicide formulations which reduce its leaching (1, 2) and for cleanup of contaminated water (3) is promising. In the current study the removal of anionic (imazaquin, sulfentrazone) and neutral (acetochlor) herbicides from water by micelles adsorbed on montmorillonite was studied. Micelles of octadecylammonium bromide (ODTMA) and benzyldimethylhexadecylammonium chloride (BDMHDA) were used. Maximal adsorption of BDMHDA on montmorillonite was 150% above the cation exchange capacity of the clay. ODTMA micelles removed 99% of sulfentrazone from water (concentration of herbicide was 33.3 ppm) at 2.5 mmol ODTMA and 2g/L clay suspensions. The binding of sulfentrazone molecules to micelles of ODTMA and sulfentrazone molecules was very strong: only 0.3% of the herbicide was desorbed by distilled water after 24 h; the pH decreased from 5.38 (pH of pure herbicide) to 4.55 (micelle with herbicide). The pH decrease and strong binding can be explained by the dissociation of sulfentrazone molecules and formation of ionic pairs between anionic form of herbicide and positively charged sites of ODTMA micelles. Imazaquin containing aromatic rings were better removed by the structurally compatible micelles of BDMHDA which also include an aromatic ring. The most effective combination of micelle and clay concentrations was 12 mM of BDMHDA and 10g/L clay: 91.6% of imazaquin (8.3 ppm) were removed from water by BDMHDA micelles versus 72.7% of imazaquin removed by ODTMA. Removal of acetochlor from water by both types of micelles was almost the same; BDMHDA micelles were slightly more efficient: 92.7% of acetochlor (33.3 ppm) were removed by BDMHDA and 90.1% was removed by ODTMA. Our results demonstrate that the micelle-clay system is efficient for the removal of contaminants from water. The efficiency of water purification requires compatibility of head groups of the molecules composing the micelles and those of the contaminants and optimal combination of concentrations of micelles and clay suspensions.

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DIFFERENTIAL THERMAL ANALYSIS (DTA) OF ORGANO-CLAY COMPLEXES IN AIR ATMOSPHERE

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Abstract

DTA has been widely used in the study of the mineralogical composition of clay minerals in soils and sediments. This technique is normally applied simultaneously with thermogravimetry (TG). The thermal reactions include dehydration of adsorbed water, dehydroxylation and transformation of the clay to meta-phases and recrystallization of the meta-phases into crystalline phases.

The first reactions are endothermic whereas the recrystallization of the meta-phases is exothermic. In the DTA of organo-clay complexes recorded in air atmosphere, the exothermic oxidation of the adsorbed organic compounds occurs in two steps mainly between the two endothermic dehydration and dehydroxylation reactions.

From DTA study of organo-smectites carried out simultaneously with evolved gas analysis (EGA) it was shown that in the first step of the oxidation most of the hydrogen of the organic compound oxidized into water but only part of the carbon is oxidized to CO_2 . The rest of the carbon converted into charcoal located in the interlayer space. In the second step of the oxidation the charcoal is oxidized to CO_2. The oxidation reaction can be completed before the dehydroxylation of the clay but sometimes it continues at higher temperatures. The exothermic peak temperatures depend on the type of the mineral and the organic compound and on the different bondings between the adsorbed organic compound and the clay mineral. It appears that after collecting more basic data, DTA curves will become applicable for the study of the types of bonds which occur between the adsorbed organic compound and the functional groups on the clay surface as well as the fine-structure of the organo-clay complexes.

ADDITION OF IRON RICH SOURCES AS A MEANS TO CONTROL SULFIDE IN FISH PONDS

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Hydrogen sulfide is extremely toxic to fish and shrimp at concentrations below one mg/l. Sulfides accumulates in the bottom water and soil of ponds, endangering the existence of the raised fish. Mass fish mortality occurred in 2000 in a water reservoir in north Israel leading to a damage in the range of one million dollar. Sulfide reacts with iron oxide and forms insoluble iron sulfide compounds.

Clay sized hematite and magnetite (with purity above 97% of Fe_2O_3 or Fe_3O_4) originating from iron pits; and Terra Rosa soil with 6% iron oxide (Fe_2O_3) by weight were used. Between 400 and 3000 mg of the iron pit sources; and soil source equivalent of 24 and 180 mg Fe_2O_3 was mixed with 25 ml of 80 mg/l total sulfide solution and kept under anaerobic environment. After 48 hrs, total sulfide concentrations at the treatments were 3.6 mg/l for the 3.0 g soil treatment and 3.8 for the 2.5 g hematite treatment. Magnetite was not effective in reducing sulfide and sulfide concentrations were similar to the control treatment.

At another experiment, hematite and Terra Rosa soil were mixed with fish-pond sediments, to contains Fe_2O_3 equivalent of 0.5-4.0% and 0.06 –0.36 % , respectively. Thirty g of the iron-sediment mixture were incubated with 30 ml overlying water and incubated in closed vials. Soluble sulfide concentration in the overlying water above the soil was determined after 14 days. Sulfide concentration was 15.9 mg/l in the control sediment In the hematite treatment the sulfide was lowered to 5.9 and 2.8 mg/l, in the lowest and highest iron treatment, respectively. In the Terra Rosa soil treatment sulfide was lowered to 14.2 and 3.1 mg/l, in the lowest and highest iron treatment, respectively.

The results suggest that the iron oxide in the soil was more reactive than the iron pit sources. A tentative practical conclusion is that mixing of 2 kg/m2 of the pit originated hematite or 3 kg kg/m2 Terra Rosa soil, with the top 5 cm sediment layer (assuming soil bulk density of 1 g/cc) would reduced sulfide concentration by >80% within about 2 weeks.

HYDRATED HALLOYSITE IN THE GOLAN HEIGHTS

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Abstract

Hydrated halloysite (10Å halloysite) is rare in soils of semi-arid areas that have a xeric moisture regime, because the hydrated status requires constant moisture in the soil. Therefore this clay mineral is common only in clay paleosols or subsoils whose drainage is slow, and moisture is preserved.

Hydrated halloysite is the major clay mineral in basalt and scoriae-derived deep soils and paleosols of the Northern Golan Heights. The mineral, formed in 140-250 KY old scoriae in soils below a depth of ~50 cm, in a region with a winter rainfall of ~1,000 mm/a, was examined in detail.

The weathered scoriae rock fragments have a specific surface area of 362 $m^2.g^{-1}$ (as against 18 $m^2.g^{-1}$ in the least weathered fragments) and contain approximately 59% clay. The cation exchange capacity of the clay varies between 12 and 36 meq.100 g^{-1}. The halloysite is either spheroidal, lath-shaped or crinkled. The morphology of undispersed material as seen by SEM is either hexagonal/prismatic, similar to that of kaolinite, or composite, of an approximately rounded shape. This latter is made up of spherical segments, joined together by flat faces, forming aggregate-like particles. Completely dispersed samples examined by HRTEM, reveal spheroids with inner spiraling.

The mineral is Fe-rich and also contains 1-6% structural TiO_2. Si/Al ratios are 2.1-2.2. It appears that the spheroidal morphology is related to the high Fe and Ti contents and to the Si/Al ratios. This is the first time that halloysite with elevated Ti contents is described.

THE EARLY DIAGENETIC ILLITIZATION OF ILLITE-SMECTITE PHASES IN CRETACEOUS SEDIMENTS AS EVIDENT FROM K-Ar DATING

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Cretaceous sedimentary rocks in Israel were sampled and analyzed in detail in search of K-bearing minerals that might give an insight into the timing of the sediment deposition and diagenesis. The study focused on two contemporaneous sections of Middle Albian to Turonian age (~104 to 90 Ma), about 40 km apart. Both sections have similar lithologies, mainly of inner- shelf shallow marine limestones, dolomites, marls, and intermediate compositions, and some sandstone and shale beds of continental origin. These sequences have not been subjected to high temperatures due to deep burial or other thermal events. Size fractions including clay fraction, fine silt fraction enriched by authigenic K-feldspar, and some coarse fractions of pure glauconite, were dated by the K-Ar method.

The most abundant clay minerals are randomly ordered illite-smectite (IS) phases of various discrete and mixed compositions in the range of 50 to 90% expandability. Illite, kaolinite, ordered IS, and palygorskite may be present. The variability in the IS composition within the vertical distance of ~150 m in both sections, as well as other evidence, suggests detrital origin for the clay minerals. K-Ar ages of clay fractions of twenty samples, of which twelve were separated into fine and coarse fractions were as follows: one clay separate yielded an age younger than the assumed stratigraphic age; five separates matched the assumed ages; five separates yielded ages older by 10% and twenty were older by up to 80% than the assumed ages, 3 – 5 fold younger than the provenance ages. The provenance ages are known from other studies and were recorded in a few coarse silt separates in the current study. This distribution of ages suggests rejuvenation of the K-Ar system in the current depositional environments, and apparently also during former cycles. These Cretaceous clays were affected by potassium-rich brines, which were produced in restricted environments on a wide shelf. The abundant potassium is evident by the intensive growth of early diagenetic K-feldspar. This is in contrast to recent deep-sea sediments, which were found to retain their provenance signatures.

Nadeau and Reynolds (1981) concluded from K-Ar ages of Cretaceous shales that random IS represents first-cycle sedimentary material formed by fixation of potassium by bentonite near the time of sedimentation. Here, the same stratigraphic K-Ar ages were obtained for clays of two adjacent beds despite the entirely different composition of the IS phases, one of which is wide-peak illite. This implies that illitization may act on different detrital IS and not only on volcanogenic discrete smectite. However, in most cases the ambient temperatures did not allow a completion of the reset process. The wide-peak illite might be a precursor of the ferrous-illite type of the Purbekian from the Jura and of the Albian-Cenomanian from Belgium, which were recently dated to yield ages somewhat younger than the stratigraphic ages (Deconinck et al., 2001; Yans et al., 2001).

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CLAY SEDIMENTATION ALONG THE SOUTHEASTERN TETHYAN MARGIN DURING THE RIFTING AND THE PRIMARY DIVERGENCE STAGE OF THE NEO-TETHYS (MIDDLE TRIASSIC TO LOWER ALBIAN)

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The sedimentation along the southeastern Tethyan margin of Israel region during the rifting and the primary divergence stage of the Neo-Tethys was controlled by marine transgressive and regressive cycles followed by terrestrial setting. The Middle Triassic to Lower Albian marine sequence of this stage is characterized by marl and shale rich in clay minerals, as well as by clayey beds interbedded within limestone, dolostone and lagoonal gypsum. The terrestrial rock sequence is dominated by sandstone and clayey palaeosol. The tendency of the clay mineral assemblages to change from marine to terrestrial and back is best observed in the Makhtesh Ramon section where marine and terrestrial sediments interfinger.

The marine clay mineral assemblage is dominated by R=1 and R=0 I/S types. Such interstratification types are first observed in the Middle Triassic (Ladinian) Saharonim Formation, contemporaneously to Pangaea disintegration event. Such I/S types persist in the overlying marine formations and marine intercalations of the Jurassic and the Lower Cretaceous of the Ramon section. It has been pointed out that conversion of smectite to I/S is occurred under deep burial diagenesisis. Nevertheless the results indicate that here the conversion probably took place due to the warm water and higher salinity of the shallow sea during the deposition. It seems that the detrital smectite transported from the open marine environment into the shallow sea and the adjacent lagoon was converted to I/S under such conditions. Argillized volcanic rocks from the basaltic volcanism of the sea floor and the mid-ocean ridge, that took place during the rifting and the primary ocean divergence, may have served as a source for the detrital smectite that transported to the shallow sea. Kaolinite and discrete illite accompanying the smectite in the marine sediments represents detrital input into the Tethyan margin from soil and through landscape erosion of older sediments. The terrestrial clay mineral assemblage is dominated by kaolinite and some discrete illite appears within palaeosols and sediments of the fluviatile-lacustrine environment.

CENOZOIC CLAY MINERALS OF THE BAIKAL REGION (EASTERN SIBERIA) IN RELATION WITH NATURE CHANGES

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Regular changes in composition and paragenesis of clay minerals within the weathering crusts and correlative sediments have been established in the Cenozoic stratigraphic-section of the Baikal Region (BR) (1, 2, 3).

Cretaceous-Paleogene weathering crust is of the kaolinite-lateritic type. The correlative sediments (kaolinite clays formed in humid landscapes) are characterized by kaolin-gibbsite horizons that substitute coal-bearing series.

The weathering crust of montmorillonite type is determined to be from the Late Oligocene-Miocene period. Smectites (di- and tri-octahedral varieties) with admixtures of kaolinite and illite dominate in the correlative sediments.

Red montmorillonite-illite weathering crusts are typical of the Late Miocene-Pliocene stage. Sediments are mainly red-colored often containing the carbonates formed during subaerial diagenesis. Smectites and illites predominate among the clay minerals.

Palaeo-soils are similar to the modern cinnamonic Mediterranean soils. In cinnamonic, red-cinnamonic and fersiallitic (= red-Mediterranean) soils hydromica and Vertisols (= tirs, smolnitza, smonitza) - essentially montmorillonite soils - predominate. Similarity established allows Mio-Pliocene palaeoclimate reconstructing in BR. There are traces of the synthesis of clay minerals (montmorillonitisation of kaolinite, abundance of X-rays amorphous substances, and the structure imperfection) in palaeo-soils.

Polymineral composition and the weathering crust of crumbly type without essential chemical-mineral transformation, characterize Quaternary sediments formed under conditions of moderate and nival climates.

Clay fraction of sediments is represented mainly by illites and smectites, whereas caolinite and chlorites are represented as admixtures. In some cases there are micas, feldspars, quartz, and amphiboles in the fraction < 0,001 mm. Coarse fractions are evidently polymictic. Quaternary palaeo-soils are of coarser grain size compared to the ambient sediments.

Composition of Cenozoic clays closely correlates with the type of weathering crust. Evolution of their composition is mainly caused by transformation of weathering processes related to the climatic changes from wet tropical in the Cretaceous-Paleogene to dry sub-tropical (Mediterranean) in the Pliocene, and moderate - cold (glaciations) in the Quaternary (3, 4). Relief changes from peneplain in the Cretaceous-Paleogene to weakly partitioned in the Miocene-Early Pliocene and highly partitioned in the Quaternary are also of great importance (3).

Two stages of epigenesis – stadial and superposed (5) – lead in some cases to anomalous distribution of clay minerals along the stratigraphic cross-section thus disturbing previously formed evolutionary-genetic branch: caolinite-smectite-illite.

Clay minerals were formed not only in the weathering crust - they have been synthesized within palaeo-soils and in alkaline waters of small warm lakes characterized by setting of authigenic carbonates; their formation could be also related to the gas-hydrothermal discharges.

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UNDERSTANDING THE COMBINED EFFECT OF pH AND TEMPERATURE ON KAOLINITE DISSOLUTION RATE UNDER ACIDIC CONDITIONS

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The main goal of this study is to demonstrate a new law describing the combined effect of pH (0.5 to 4.5) and temperature (25°C to 70°C) on kaolinite dissolution rate, under far from equilibrium conditions, as a step towards establishing the full rate law of kaolinite dissolution under acidic conditions. Dissolution experiments were carried out using non-stirred flow-through reactors fully immersed in a thermostatic water bath held at a constant temperature of 25.0°C, 50.0°C or 70.0°C ± 0.1°C. Kaolinite dissolution rates were obtained based on the release of silicon and aluminum at steady state. The results show good agreement between these two estimates of kaolinite dissolution rate. In general, kaolinite dissolution rate increases with temperature and decreases with pH (Fig. 1).

The combined effect of pH and temperature is modeled by two independent proton promoted reaction paths:

(1)

$$\frac{Rate}{\rho_r} = A_1 \cdot e^{-E_{a_1}/RT} \cdot \frac{K_{0_1} \cdot e^{-\Delta H_1^0/RT} \cdot a_{H^+}}{1 + K_{0_1} \cdot e^{-\Delta H_1^0/RT} \cdot a_{H^+}} + A_2 \cdot e^{-E_{a_2}/RT} \cdot \frac{K_{0_2} \cdot e^{-\Delta H_2^0/RT} \cdot a_{H^+}}{1 + K_{0_2} \cdot e^{-\Delta H_2^0/RT} \cdot a_{H^+}}$$

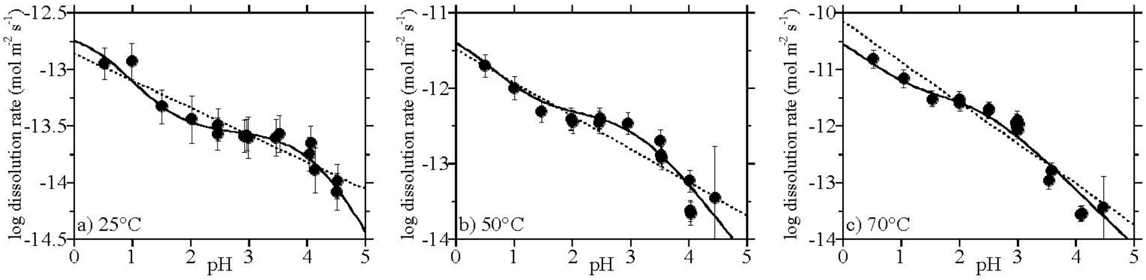
where ρ_r (mol m^{-2}) is the density of reactive surface sites on the mineral surface, A (s^{-1}) is the pre-exponential factor, E_a (kcal mol^{-1}) is the apparent activation energy, K_0 (M^{-1}) is a constant related to the entropy of the proton adsorption, ΔH^0 is the net enthalpy of adsorption, a_{H^+} is the activity of protons in the solution, R (kcal mol^{-1}) is the gas constant, T is the temperature (K) and the subscripts 1 and 2 refer to the first and second reaction paths, respectively. The parameters in the rate law were determined by fitting the entire data set of kaolinite dissolution rates to equation (1) using a multiple non-linear regression. The resulting rate law is:

(2)

$$Rate = 2 \cdot 10^2 \cdot e^{-22/RT} \cdot \frac{2 \cdot 10^{-10} \cdot e^{19/RT} \cdot a_{H^+}}{1 + 2 \cdot 10^{-10} \cdot e^{19/RT} \cdot a_{H^+}} + 5 \cdot 10^7 \cdot e^{-28/RT} \cdot \frac{1.4 \cdot 10^{-7} \cdot e^{10/RT} \cdot a_{H^+}}{1 + 1.4 \cdot 10^{-7} \cdot e^{10/RT} \cdot a_{H^+}}$$

A comparison between the prediction of equation (2) and the experimental data at 25°C, 50°C and 70°C is shown in Fig. 1. The first reaction path controls the overall dissolution rate at pH≥2.5, whereas the second path controls it below pH 0.5. The two reaction paths influence the rate between pH 0.5 and 2.5.

Fig. 1: Variation of log dissolution rate with pH: (a) at 25 ºC, (b) at 50 ºC and (c) at 70 ºC. The dashed curves and the solid curves are a result of linear regression to the data at each plot and multiple non-linear regression of equation (1) to the entire data set, respectively.



Si-ASSOCIATED GOETHITE IN HYDROTHERMAL SEDIMENTS OF THE ATLANTIS II AND THETIS DEEPS, RED SEA

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The properties of Si-associated goethite from sediments in the Atlantis II and Thetis Deeps in the Red Sea have been investigated in order to determine the effect of Si on the mineral. Two types of morphologies dominate in most samples: multi domain crystallites, probably due to elevated Na concentration in the initial brine from which the mineral had crystallized, and mono-domain, acicular crystals. Goethite crystals with elevated Si/Fe elemental ratios are usually smaller and poorly crystalline, exhibiting numerous crystal defects, whereas larger crystals with higher crystallinity have lower Si/Fe elemental ratio. The higher Si/Fe ratios in Atlantis II Deep goethites and the lower ratio in Thetis Deep goethite probably reflect the levels of Si concentration in the hydrothermal fluids from which goethite precipitated. At relatively low Si/Fe ratios, the major effect of Si is to retard growth of the crystallites, but only a small number of defects is formed. At high Si/Fe ratios the defect concentration affects the properties of the crystals, as observed with Mössbauer spectroscopy. Si association with goethite effects primarily crystal size as indicated by X-ray diffraction and infrared spectroscopy.

IMPROVED METHODS FOR SELECTIVE DISSOLUTION OF MANGANESE OXIDES FROM SOILS AND ROCKS BY HYDROXYLAMINE HYDROCHLORIDE AND HYDROGEN PEROXIDE

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Abstract: Hydroxylamine hydrochloride and hydrogen peroxide have been used in the past for selective dissolution of Mn oxide minerals. The methods reported in the literature, however, exhibit low percentages of manganese release. The present study was intended to improve the methods proposed in the past with this regard. An approach of determining the stoichiometry of the reactions was used in the present study. According to the stoichiometric considerations, incomplete dissolution of Mn oxides reported in the literature is due to the lack of hydroxylamine hydrochloride added or due to the lack of acid added in the case of hydrogen peroxide treatment. By using higher solution/solid ratio in the case of hydroxylamine hydrochloride and by increasing the acid concentration in the case of hydrogen peroxide treatment, very rapid and complete dissolution of synthetic manganese oxides was obtained. Kinetics of dissolution of natural samples, however, was slower than that of synthetic ones. Based on the results obtained, the improved methods are as follows: (1) 0.1 N hydroxylamine hydrochloride, non-acidified, 2 hours of stirring, solution/solid ratio of 2000; (2) 30% hydrogen peroxide in 0.5 N nitric acid, 0.5 hour of stirring, solution/solid ratio of 1000. With the improved methods almost complete release of manganese from samples was achieved without decreasing the selectivity of dissolution, i.e. without dissolving significant amounts of iron oxides and other minerals.

APPRAISAL OF BENTONITE DEPOSITS: A CHALLENGE FOR THE RESOURCE GEOLOGIST

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Bentonites are clays consisting essentially of smectites irrespective of their mode of origin. Due to their unique physical and chemical properties they are utilised in a variety of industrial applications, including foundries, oil drillings, civil engineering and environmental applications animal litter etc. Prospecting for bentonite deposits begins with the recognition of the raw material in the field. A simple guide for recognition of a bentonite is the "pop-corn" texture resulting from consecutive swelling and contraction. In several occasions bentonites form beds, stratigraphic markers, often used for geological correlation, but hydrothermal deposits often form irregular bodies controlled by tectonics. A high quality bentonite should be compact, soft and soapy to the feel and its colour varies considerably according to the nature of the parent rock, the geological history and the location of the deposit with respect to the surface (burried or exposed).

Confirmation of any field recognition is made using mineralogical techniques the most important of which is X-ray diffraction (XRD). XRD will assist to distinguish pure smectite from mixed layer illite smectite (IS). Separation of the two phases may require an experienced clay mineralogist if the IS displays random interstratification especially at low illite content. Possible existence of illitic layers in the clay fraction deteriorates physical and chemical properties of bentonites. Typical commercial bentonites containing random mixed layer illite-smectite (K-bentonites), exist in the USA (Otay type-California), Greece (Milos) Cyprus etc. XRD investigation may be complemented by other techniques such as thermal analysis, IR spectroscopy, and electron-beam techniques (SEM, TEM-AEM and EPMA).

The importance of a proper mineralogical investigation of a bentonite deposit must not be overemphasized because the behaviour of the clay in the industrial applications depends on the structure of the smectite and the other minerals present. In order to assess a bentonite deposit the terms quality and grade are used separately in contrast with other raw materials . In the context of bentonites the term quality refers to the performance of the material in its different applications while the term grade refers to the smectite content of the bentonite. The quality of a bentonite can be assessed in the laboratory by sodium carbonate exchange and determination of the swelling efficiency (swelling index) and/or of the liquid limit. Although with these tests the optimum carbonate addition is determined, usually in industrial practice optimum sodium carbonate addition varies in different applications. The grade of a bentonite can be assessed by measurement of the cation echange capacity (CEC) and/or its total specific surface area usually with EGME. Both quality and grade can be affected by geological factors after formation of the bentonite. Important factors are hydrothermal alteration and/or diagenesis. For instance grade is affected by illitization or kaolinization of smectite, by formation of smectite with different layer charge and/or by formation of not-smectitic minerals. Quality is also affected by lowering of the pH of bentonite, by formation of smectite with different layer charge and/or different lattice dimensions. Although in general a high grade bentonite has also high quality, post-depositional geological history has resulted in significants exceptions.

Evaluation of quality and grade is appropriate for preliminary assessment of a bentonite and with suitable sampling the variability of the material within the deposit can be established. Also it provides valuable data on the overall properties of the clay from which potential uses can be inferred. Further tests on bentonite are mostly unique to individual industrial users (eg. viscosity and fluid loss for drilling muds, bonding strength for foundry uses, white colour in filler industry etc) or may require trials on use. These tests are often defined in industrial standards or/and national or international ones, which must be met by the raw materials.

THE CHANGE OF PHASE COMPOSITION IN KAOLINITE- AND ILLITE -RICH CLAY BASED CERAMIC BODIES

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Abstract

The three clays which are representative of the high kaolinitic HB, illitic KW and naturally mixed kaolinite–illite P1 clays of Westerwald area are selected for this study. They are mixed with each other and also with K, and Ca -Na feldspar. The high temperature phases of the mixed bodies are considered into three groups; crystalline phases, amorphous/glassy phases and porosity. The mixed bodies mainly consist of kaolinite, illite, quartz and feldspar. Therefore the aim of this study conducted to determine;the effect of kaolinite/illite/quartz ratios, -the effect of heat treatment and -the effect of feldspar addition on fired mineralogy. For this reason, it is primarily essential to know which crystalline and noncrystalline phases and how much of each of them are present in the fired bodies. For this purpose systematic sampling and the experimental investigations were carried out on these clay mixtures. Understanding of these effects provides the most important pre-condition: optimum raw material composition for the production of high quality ceramic bodies. In this respect, modification of heat treatment and feldspar addition are mainly directed towards improving the ceramic body structure. The crystalline phases were determined as cristobalite, mullite, quartz, hematite and anatase. The tendency to mullite and cristobalite formation is very distinctive in kaolinitic clay, and the structure is dominated by the spiky primary mullite. In the illite/sericite-rich KW mixtures, the higher K content causes a large amount of melt superimposed on the primary mullite formation. The cristobalite formation is completely suppressed in illite/sericite-rich KW bodies. After dehydroxilation, metakaolinite and illite-sericite anhydride structures are formed. The persistence of illite/sericite anhydride peaks above 950°C in KW clay indicates the presence of sericite/muscovite mineral. The disappearance temperatures of K-and Ca-Na feldspar lines within the XRD patterns of mixed bodies are different. K-Feldspar lines disappear earlier in HB bodies than as in KW bodies, and Ca-Na feldspar shows a reverse behaviour.

EFFECTS OF CALCIUM HYDROXIDE ON CASTING PROPERTIES OF CERAMIC CLAY SUSPENSIONS

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Abstract

The aim of this study was to investigate the casting properties of white ware ceramic slurries in the presence of calcium hydroxide. For this purpose the recipe that contains 24% feldspar, 24% quartz, 35% ball clay and 17% clay was prepared through the experiments. Influence of calcium hydroxide on the properties of the above recipe was studied at different concentrations ranging between 0.06 to 0.08 %. Also sodium silicate was used together with the calcium hydroxide for the slurry preparation. Similar experiments have been performed by using sodium carbonate and sodium silicate for comparison purposes. To investigate the effects of these two chemical agents viscosity and casting rate measurements were made. Physical properties such as strength of materials water absorption, shrinkage in green and sintered forms were measured to understand the effect of calcium hydroxide on the whiteware ceramic slip body.

Results indicated that the use of calcium hydroxide caused some significant improvements in casting behavior of the slips. According to the outputs of the study, in the case of slurries contain calcium hydroxide and sodium silicate casting rate is higher than the slurries contain sodium carbonate and sodium silicate.

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A CONTRIBUTION TO THERMAL STUDIES OF THE MIXED SALT-CLAY ROCKS

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The authors' work carried out in last 5 years enables to improve the application of the thermal analysis in the studies of very mixed rocks consisting of salt-, clay- and carbonate minerals and of organic matter. The results of this work proved that the most important factor of TA is to ensure the possibility of maximum free escape of gaseous reaction products and O_2 diffusion into the analysed sample layer.

Such a procedure facilitates the distinction of water liberated at low temperatures from OH groups from clay minerals. It also enables the recognition of differentiated linking of OH groups in clay minerals as well as detailed determination of carbonate minerals and organic matter admixtures.

These results have been confirmed by X-ray and IR investigations. Their additional implication is the need of some modifications in the redesigning the TA equipment.

THE USEFULNESS OF Ta IN THE INVESTIGATION OF Fe-SUBSTITUTION IN Mg-CHLORITES

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The results of authors' previous works (1, 2) as well as the methodological recommendations by F. Paulik (3) have been the basis for the initiation of the application of the OTA method for the investigation of Permian zubers (mixed salt-clay rocks). The OTA analysis carried out on a large number of samples allowed to determine their differentiated clay minerals composition. These results completed by X-ray investigation of selected distinctly different samples served for detailed determination of sedimentary chlorites.

The temperatures of the characteristic endothermic effects of OH groups liberation and of exothermic reactions of olivine formation were used as the criterion.

In concluding it was found that Mg-chlorites with Fe-substitutions occur in the zubers investigated.

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THE USE OF LONG-CHAIN ORGANO-CLAYS FOR SORPTION OF HIGHLY HYDROPHOBIC COMPOUNDS AND FOR THE TREATMENT OF INDUSTRIAL WASTEWATER

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It is generally assumed that short-chain adsorptive organo-clays, such as tetramethylammonium clay, sorb non-ionic organic compounds much better than long-chain partitioning organo-clays like hexadecyltrimetylammonium clay. However, this concept was based mainly on series of studies[1,2], mostly done with low molecular weight organic compounds (with low to medium hydrophobicity), while very little data were published on the sorption of highly hydrophobic organic compounds on the above mentioned organo-clays.

We suggest that for highly hydrophobic compounds the above mentioned concept is not valid and that the opposite is true, i.e. that the long-chain organo-clays will be much better sorbents than the short-chain organo-clays because of their stronger hydrophobic nature.

To examine our hypothesis, the sorption of seven compounds (six pesticides and one polyaromatic hydrocarbon) with various hydrophobicities (Log Kow 2.5 - 6) were studied on tetramertyltriamonium- and octadecyltrimethylammonium-bentonite, representing short and long-chain organoclays, respectivly. The sorption experiments were carried out with individual pesticides in tap water, and in industrial wastewater that were sampled from a pesticide manufacturing plant.

As initially proposed, compounds with low or medium hydrophobicities (Log Kow 2.5 - 3.8) were sorbed better on short-chain organo-clays, but the more hydrophobic compounds (Log Kow 4.8 - 6) sorbed better on the long-chain organo-clay. The same sorption preference was observed in wastewater, as the less hydrophobic compounds sorbed better on the short-chain organo-clays while the more hydrophobic compounds sorbed better on long-chain organo-clays.

When the sorption experiments were repeated in industrial wastewater that in addition to the pesticides (0.1-10 mg/l), contained also industrial solvents (methanol, trichloroethylene etc.), and raw materials (such as amines) the sorption of pesticides on long-chain organo-clays, was very simillar to that observed in tap water. However, the sorption of pesticides on short-chain organo-clays was significantly suppressed in wastewater compared to tap water. This can be attributed to the competitive nature of sorption to short-chain organo-clays.

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RED CLAYS FROM CENTRAL AND EASTERN CRETE – GEOCHEMICAL AND MINERALOGICAL PROPERTIES IN VIEW OF PROVENANCE STUDIES ON ANCIENT CERAMICS

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Chemical studies on the provenance of ancient ceramics are based on the assumption that pottery produced from the same clay paste shows a similar chemical composition, while it is distinguishable from that produced from a different paste. In this way, pottery can be assigned to particular production groups, and ascribed to an origin by comparison with other analyses. Raw material is usually not suitable for use by potters, without some sort of modification. Such processes include levigation, tempering with non plastic materials, and mixing with other clays. Therefore, in most cases, ceramics are difficult to match directly with the chemical composition of a distinct clay source. Instead, reference material - ceramics of known or assumed origin - is used to ascertain the place of production.

Nevetheless, the raw materials used in the production of a given ceramic comprise the initial source of compositional variability in any given ceramic paste. It is, therefore, imperative that we gain a greater understanding of natural variability of clay rich and other deposits used in the process of ceramic production.

The present study of red clay deposits is part of a larger study of clay sources in Crete, examining natural compositional variability within clay sources and between sources of similar clay types [1]. The study was motivated by the close chemical similarity of certain types of Bronze Age ceramics from Central Crete, which petrographic study suggests were produced in different locations, using different clay pastes.

A total number of 17 samples of clayey materials were taken from seven deposits in Central and Eastern Crete. Geologically the deposits can be classified as Quaternary alluvial red beds, except for one deposit, which is an authigenic clay deposit. The samples were analysed by XRF and NAA for the determination of 32 major, minor and trace elements. Additionally, the variation of the mineralogical composition was examined by XRD and grain size analysis. The resultant data are compared with those from other clay types from the same area and with analysed red clays from Western Crete.

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CLAY MINERALS DISTRIBUTION AND LAND USE OF VOLCANIC SOILS IN MIDDLE ITALY

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Central Italy is characterized by a series of extinct volcanoes, mainly of pleistocenic age, the deposits of which outcrop for a few thousands of square kilometres. In the Latium region, the Vico volcano, with a caldera partially infilled by a lake, represents an ideal environment for studying the interaction among different types of volcanic materials, bio-climatic and morphologic factors and the influence of man's activity on pedogenesis and clay formation. The soils formed from the weathering of these materials, like other soils of volcanic nature, present physical and chemical properties favourable for use in agricultural and forestrt. The andic properties show a gradient in function of climatic variation linked to morphologic factor (altitude, exposure, topographic position) that are also reflected at taxonomic levels (climatosequence) (1). Similarly, the parent material has an effect on the pedogenesis: namely the compactness or cementation (zeolitization) of pyroclastic flows favoured in fact neogenesis of crystalline clays, whereas loose or highly vesicular materials could be more weathered into amorphous products (allophane). Meanwhile the predominant influence of climate, natural vegetation and parent material on clay genesis, the anthropic factor of land use takes a part in modifying the existent equilibria, especially whenever a situation of transition or a co-existence of different pedogenetic processes have occurred. As a rule one can affirm that genesis of amorphous clay has predominated in the highland, between 600 and 900 m a.s.l., characterized by the presence of monospecific and multistratified beech or oak forest and a mesothermic moist climate. In these cases of negligible anthropic disturbance, the microclimatic variation linked to slope exposure has determined the type and the quantity of amorphous products: prevalence of Al-humus complexes on the allophane in the surface horizons of acid Andisols with melanic epipedon (Typic Melanudands) in the wetest and coldest sites; dominance of allophane with respect to Al-humus complexes in the differentiated Andisols with Bw horizon in the sites characterized by a higher insolation at southern slopes (Typic Hapludands) (2). On the external slopes of volcanic apparatus, beneath 600 m of elevation, the anthropic influence has revealed oneself in the management of chestnut wood, both for periodical cutting and harvest of the fruit, whose presence can be brought back to the alteration of the original mixed wood *(Quercus-Tilia-Acer)*. In this environment, characterized by a higher insolation and disturbance of more superficial horizons, the andic properties are lesser: it is the domain of andic brown soils (Andic Dystrochrepts). In these soils the amorphous Al-humus complexes disappear or decrease to a very low amount; also the allophane decreases and halloysite at 0.7 and 1.0 nm becomes the main constituent. Near the topsoil halloysite is prevalently in dehydrated form (0.7 nm) and appears in curled flakes, whereas in deepth it becomes more spherical and hydrated (form at 1.0 nm). Where the parent material was constituted by a cemented tuff from pyroclastic flow or phreatomagmatic eruption, the compactness of the rock, which causes the confinement of solutions, produces the weathering of the glass of pumices directly in spherical halloysite at 1.0 nm (3). Finally, the large ignimbritic plateau downwards is the more anthropized area, where the winter wheat and the specialized growing of hazelnut constitute the prevailing land use. In this environment the temperate moist climate with dry summer and the land use favour the moistening-drying cycles ledding to conspicuos neogenesis of crystalline clays (0.7 nm halloysite and some smectites) and their translocation through the soil profile. It is the domain of Alfisols.

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MONAZITE ALTERATION MECHANISMS AND DEPLETION MEASURMENTS IN KAOLINS

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Two kaolin deposits in Greece were studied in order to compare the impact of the alteration mechanism to the presence of rare earth elements in the deposits and to find a measurement for the depletion during the alteration processes. Halloysite and kaolinite coexist in gneissic weathering profiles, under a temperate climate as found in the Leucogia area NE Greece [1]. Kaolin occurrences of Kos island, Aegean sea, Greece, are products of hydrothermal alteration of rocks of rhyolitic composition. The mineralogy of primary rocks and kaolins was investigated by X-Ray diffraction (XRD). In order to resolve the genetic relationship between monazite and its alteration products microtextures were examined by scanning electron microscopy (SEM) using thin sections and chips from the raw samples; their chemical composition was determined using a Scanning Analytical Electron Microscope (SAEM) fitted with EDS and WDS. Bulk rock chemical analyses were performed in order to correlate major and trace elements behaviour with the alteration mechanisms.

Monazite [$(Ce,La,Nd,Th)PO_4$] is an accessory mineral and the only mineral that contains lanthanum, cerium and neodymium in both areas and in addition thorium in the Leucogia area. The presence of monazite was not detected by XRD, due to its accessory character, but was verified with the use of SAEM. Monazite (Ce), in the gneissic weathering profiles of the Leucogia area, is partially altered to a Th-OH silicate microcrystalline phase with very low concentrations of LREE. The relict monazite crystals are depleted in thorium and lanthanum. The depletion and/or the enrichment of the various elements in the bulk sample appear to be related to mineral breakdown rather than to mild leaching of primary minerals by meteoric water. The only element that is apparently immobile is thorium so this element can be used as a measurement for the depletion in this environment.

Monazite (Ce), in hydrothermaly altered rhyolitic rocks of Kos island, is altered to P-bearing crandallite-goyazite. During this alteration process LREE are depleted. Hydrothermal fluids add to the altered rhyolite significant amounts of Sr, Cr, Cu, Zn and Fe. Relative to the parent volcanic rock (rhyolite), the kaolinitic zone is characterized by depletion in Si, Na, K, Ca, Ba and enrichment in Al, Sr, P and Fe [2]. Phosphor is accommodated exclusively in the monazite structure, it was found to be the only element with an immobile behaviour, it is therefore suggested that P may be used as a measurement for the depletion in this hydrothermal environment.

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ASSIGNMENT OF BANDS TO TRANSVERSE AND LONGITUDINAL OPTICAL MODES INVOLVING IN-PHASE VIBRATION OF INNER-SURFACE OH-GROUPS OF KAOLINITE

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An IR-spectroscopic study of kaolinite samples collected from the Ukrainian Shield was conducted. Kaolinite samples of different degree of dispersion were investigated in shells or medium with different values of dielectric permittivity ϵ_m *(from 2.33 to* $\approx$ *1.51)*. The sizes of coherent scattering regions along the "c" axis were determined using the method of fourth central moments by diffraction reflexes widening and were from 10 to 70 nm. One partially deuterated sample (up to 10-15%, significance level – 0,05) with size of coherent scattering regions < 10 nm was also investigated.

It was shown that the absorption band at $\approx$ 3680 cm^{-1} labeled as a Z-band in [1] is observable in IR-spectra without using a procedure of bands contour decomposition into five components in the region 3600-3700 cm^{-1} and also without using a photoacoustic method of registration. The intensity of Z-bands in IR-spectra (as well as in Raman-spectra [1]) is correlated with sizes of coherent scattering regions along the *"c"* axis where the domain of coherent scattering is extended into the whole particle thickness; otherwise the correlation is broken. Almost all known methods of samples preparation are suitable for Z-band registration with different degrees of resolution except for the KBr-pellets method. Use of the KBr-pellet method used for sample preparation is the reason that this band was discovered in IR absorption spectra somewhat later [2] than in Raman-spectra [3].

It was also shown that an additional band at $\approx$ 3640 cm^{-1}, unknown earlier, is found in IR-spectra of kaolinite. Within the region of 3650-3675 cm^{-1} a more complex set of closely located bands is observed in addition to two known bands at = 3650 cm^{-1} (C) and = 3670 cm^{-1} (B). The location of A-band maximum doesn't correspond to the calculated direction of Fröhlich mode frequency shift following from formula $\epsilon = \epsilon_m(1 - \frac{1}{L})$ (*L* – geometrical factor of particle) at increasing ϵ_m values up to 2.33.

It was established for partially deuterated samples that:

- significant differences (according to Fisher-Snedecor criterion) of dispersion for OH-band intensity in the maximum at 3695 cm^{-1} compared to that of the original sample (KBr-tablets),
- distinct absorption at 3680 cm^{-1} as an individual band (thin layer coating upon CaF_2 – plate).

Results obtained from kaolinite in transparent (for this IR region) shells confirm that all the unit-cell vibrations are active in IR-spectra as well as in Raman-spectra [4]. However, they allow us also to suppose that Z- and A-bands don't represent frequencies of transverse and longitudinal optical modes of in-phase coupled vibration of the same inner-surface OH-groups of the unit cell but have a different origin (interpretation).

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TECHNOLOGY AND COMPOSITION OF ROMAN POTTERY IN NORTHWESTERN PELOPONNESUS, GREECE

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Roman ceramic workshops which were excavated in the area of Patras (NW Peloponnesus) are connected with the economic flourishing of Patras during the Roman period (1st – 3rd c. BC). [1]

Historical and archaeological sources suppose that Roman period potters used imported raw materials from South Italy or Ancient Corinth (NE Peloponnesus). However, clay mineral assemblages are common in the Plio-Pleistocene sediments of Northwestern Peloponnesus [2] and a good number of modern ceramic centers are operating in the area.

In order to establish the provenance of raw materials, 100 representative samples of fine ceramic lamps from the two excavated workshops were collected. One of the workshops produced red-painted and the other unpainted lamps. Red-painted and unpainted samples were grouped according to the colours of their ceramic bodies. The colour of the ceramic body of red-painted lamps varies from light brown, red, reddish yellow to pink whereas the colour of the unpainted ones varies from gray, grayish brown to olive yellow in the Munsell' s system. [3]

Optical microscopy was applied for the characterization of the clay fabrics of the ceramics. The majority of the samples show a fine-textured fabric with a few aplastic grains and a varying degree of vitrification. These aplastic grains are subangular to subrounded, silt sized, composed mainly of quartz, plagioclase, K-feldspar and calcite. Additional grains in the fabric include biotite, chlorite, muscovite and disseminated iron oxides. The clay fabrics of the samples from the red-painted lamps producing workshop are distinguishable in two groups, according to the percentage of the minerals (calcite, biotite, muscovite) present.

ICP-MS major elements analysis from 50 samples indicate that all the ceramic bodies are composed of a Fe-rich calcareous clay, although it is suggested that the ancient potters used in fact a fine clay with natural temper or a mixture of clays from different sources. X-Ray diffraction (XRD) and Scanning Analytical Electron microscopy (SAEM) study, mainly of the clay matrix, leads to the distinction between primary minerals, prograde minerals formed after the firing process, and secondary minerals formed after the burial processes. The preservation of clay minerals (illite, chlorite, smectite and their mixed-layer) in some samples and the presence of prograde minerals (augite, gehlenite) in others, indicate differences in firing temperatures.

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CLAY SEDIMENTATION ALONG THE SOUTHEASTERN TETHYAN MARGIN DURING THE PROGRESSIVE DIVERGENCE STAGE OF THE NEO-TETHYS (UPPER ALBIAN TO TURONIAN)

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The sedimentation along the southeastern Tethyan margin of Israel region during the progressive divergence stage of the Neo-Tethys took place in an epeiric sea that covered the passive continental margin. The large marine transgression began at the Upper Albian and came to an end in the late Middle Eocene. The Upper Albian to Turonian marine sequence of the divergence stage is characterized by marl and shale rich in clay minerals, as well as by clayey beds interbedded within limestone and dolostone.

The base of the marine transgression, the Albian Hevyon Member, is marked by sandstone and limestone rich in glauconite. R=0 type I/S and kaolinite are major clay minerals in sediments deposited on the shallow-shelf platform. R=1 type I/S is present in sediments of the extending lagoon. The shallow-shelf clay assemblage appears within the dolostone and the marl of the Cenomanian Bet Meir Formation and the En Yorqeam Member in the Judea and Negev regions. On the other hand, smectitic I/S, very rich in smectite layers and palygorskite are major clay minerals in sediments deposited, contemporaneously to these rock units, on the outer shelf in the open marine environment. The outer shelf clay assemblage appears within the chalk of the Cenomanian Isfiye and Khureibe Formations in the Mount Carmel area. Pedogenic palygorskite is found in a Turonian clastic unit in the Negev region.

The composition of smectitic I/S in the open marine sediments support the idea that transportation from the open marine environment into the shallow sea and the adjacent lagoon is the source of the detrital smectite converted to I/S. Possible neoformation of orderly-interstratified illite/smectite on deep burial diagenesis is rejected. Some detrital input from the continent is the source of kaolinite and discrete illite accompanying the smectite in the sediments. Participation of palygorskite during the Cenomanian is related to conditions of warm and hypersaline bottom waters. Heavy brines from the shallow-shelf platform lagoon extending southeast probably moved along the bottom of the outer shelf on which the Isfiye and Khureibe Formations were formed and stimulate the participation of the palygorskite. The pedogenic palygorskite in the Turonian clastic unit represents episode terrestrial conditions of soil development or extending playa.

CLAY SEDIMENTATION ALONG THE SOUTHEASTERN TETHYAN MARGIN DURING THE CONVERGENCE STAGE OF THE NEO-TETHYS (SENONIAN TO EOCENE)

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The sedimentation along the southeastern Tethyan margin of the Israel region during the convergence stage of the Neo-Tethys took place on sea-bottom topography following the main folding of the Syrian arc deformation belt. The Senonian to Eocene marine sequence of this stage was deposited in a dipper marine environment during a marine transgression that caused the sea to extend to 600-1000 km south-east of the present coast and to cover the fold topography. Thick units are widespread mainly within the synclinal basins. Vast amounts of smectite-rich clayey sediments were deposited during the Upper Senonian and the Paleocene. The clayey units of the Paleocene are prevalent throughout the Middle East.

Smectitic I/S, very rich in smectite layers, is the common type in marine sediments. Such I/S type is predominant in the chalk of the Santonian Menuha Formation and in the phosphorite of the Campanian Mishash Formation. I/S-kaolinite assemblage is prevalent in the marl of the Maastrichtian Ghareb Formation and in the shale of the Danian part of the Taqiye Formation. I/S-palygorskite assemblage with occasional sepiolite is prominent in the shale of the Landenian part of the Taqiye Formation and within the limestone of the Lower Eocene Mor and Adullam Formations.

It seems that the Smectitic I/S was transported to the basins from the open marine environment. However, in the dipper marine environment of the basins, the smectitic was not converted to a higher interstratification type. Argillized volcanic rocks from the andesitic volcanism of an island arc that took place during the ocean convergence due to plate subduction, may have served as a source for the detrital smectite that transported to the basins. Some detrital input from the continent is the source of kaolinite and discrete illite accompanying the smectite in the sediments. Participation of palygorskite and occasionally sepiolit during the Landenian and the Lower Eocene is related to conditions of warm and hypersaline bottom waters due to the development of stratified water bodies in the restricted synclinal basins.

ADSORPTION OF DIFENZOQUAT TO MONTMORILLONITE

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The main aim of this study was to investigate the feasibility of employing difenzoquat (DZ), which is an approved monovalent cationic pesticide in enhancing the biological activity and reducing the applied amounts of dipyridyl contact herbicides, such as the divalent organic herbicide diquat (DQ), or combined diquat/paraquat(PQ) herbicides (Weedol©) whose activities can be significantly reduced due to their adsorption by dust particles accumulated on leaves of weeds(1). The idea was that competition of DZ with DQ or PQ for adsorption on the dust particles will enhance the amount of DQ available for acting on weed plants. A similar approach was used in the past to improve efficacy of dipyridyl herbicides, by adding the monovalent cations acriflavin or mepiquat(2-4). The adsorption of DZ on model clay dust, such as montmorillonite, was studied at a wide range of DZ concentrations and ionic strengths. Up to DZ loadings of 0.4 mmol/g clay (half of the CEC), all the added cation adsorbed; the amounts adsorbed were reduced by 8% in the presence of 500 mM NaCl. An adsorption model which combines electrostatic equations with specific binding in a closed system could adequately explain and predict the adsorbed amounts of DZ. Competition between DQ and DZ was also determined and the predictions of the model were examined. These predictions were adequate for total loading up to the CEC. At higher loads the amounts of DZ adsorbed predicted by the model are higher than the measured. In accord with a previous study at, a reduction in the c-spacing of the platelets by the divalent organic cation at relatively high added concentrations results in reducing the adsorbed amount of monovalent organic cations(5). The improvement of the herbicidal activity of DQ/PQ by adding DZ, was tested in a pot experiment, obtaining excellent herbicidal activity with a dose 40% lower than the minimum recommended.

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KAOLINS FROM ALVARAES (NW PORTUGAL): MINERALOGY AND BENEFICIATION WITH ULTRASOUNDS FOR PAPER APPLICATION

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In Portugal there are several kaolin deposits, both sedimentary and residual, in a coastal region N of Oporto related to granitic rocks. The main area is the so-called Alvaraes Basin, about 40km N of Oporto, where, over a kaolinized granitic basement, clays and silts as well as sedimentary kaolin, were deposited. This latter material has been used for the paper and ceramics industries and the residual kaolin, due to technical problems related to exploration, has been produced in limited quantities especially for ceramics.

These kaolins were subjected to an initial treatment stage that consisted in obtaining the <2 μm fraction with the purpose to analyze their potential for use in filler applications. In terms of mineralogical characteristics, these two kaolins are quite different. Residual kaolin has a very low viscosity, deffloculant demand, and abrasivity. In terms of color they are very similar, the residual kaolin is slightly brighter and slightly more yellow. Iron and titanium dioxide are the two most important contaminants, specially the former one. Magnetic separation and selective flocculation are the two most common beneficial treatments but an interesting alternative could be a process acting as refining and as beneficiation. So, in order to improve the properties of those two kaolins for paper applications, they were subjected to ultrasound treatments. In this process, a kaolin suspension with 76% solids was subjected to ultrasounds for one hour with an intensity of 200W with a very low content of added hydrazine hydrate. Hydrazine hydrate modifies the structural interlayer cohesion energy of kaolinite crystals while the ultrasound facilitates the aleatory rotations and translations between structural layers. This process changed the particle size distribution, specific surface area, abrasivity, and density (acting like a refining process), but also changed rheological characteristics and color, decreasing iron and titanium contents (acting like a beneficiation process).

Treated and non-treated kaolins were later subjected to a third phase in order to analyze their potentials for filler application in paper. Paper sheets (80 gm^{-2}) with eucalyptus pulp (35°SR) were produced in a dynamic former machine and four filler levels were selected: 0%, 7.5%, 15%, and 22.5%. Different properties were studied such as: structural (bulk, air permeability and smoothness), optical (opacity and light scattering coefficient) and mechanical (burst and tension).

Due to the delamination effect of ultrasounds, we were able to detect significant differences in paper properties between treated and non-treated kaolins. Treated kaolins give less bulkier, smoother sheets with greater air permeability. Optical properties were also improved, specifically sheet brightness and the light scattering coefficient while opacity was maintained at nearly the same levels. Despite the fact that treated kaolins have more fine particles caused by ultrasound treatment, which could be detrimental to mechanical properties because of the broader particle size distribution, they show the same values of burst and tension strengths than that of non-treated kaolins.

A NEW APPROACH FOR STUDYING CLAYS BY THE METHODS OF ELECTROKINETICS

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One of the most important properties of minerals is the surface charge arising when clays contact polar dispersion medium. Its origin is directly related to the genetic structure of clay mineral, the ion exchange capacity and hydrophilicity. Both properties have been thoroughly studied /1/. Concerning the surface charge, it was assessed traditionally by indirect method measuring electrokinetic potential. It had always been determined in the framework of Smoluchowsky theory, that is only fair for the case of

$$(\chi r, \chi a) \gg 1 , \tag{1}$$

where χ is Debye parameter or inverse thickness of double electric layer, r and a – radius of pore and particle correspondingly.

The well known fact of the unique clay ability to spontaneous dispersion at the moment of its contacting water is based on the genetic nature of clays. It results in particles and pores formation having so small dimensions that equation (1) is not obeyed, and Smoluchowsky theory cannot be applied, even if one accounts for the surface conductivity. Moreover, the electrokinetic effect dependence (electroosmosis in particular) on their compactness (or packing) was found out for clays. In the other words – on the volume or mass fraction of particles, if consider the concentrated suspensions, pastes, gel-like structures formed by the clays in water.

Systematical studies of clay electroosmosis versus disperse phase fraction enabled us to find out a new, never known regulations and formulate conditions allowing to define both surface charge and the bound water amount (say, hydrophilicity) based on the measurements of electroosmosis rate versus clay concentration in the system /2/.

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CLAYS IN SOILS TYPICAL OF TREBBIA RIVER BASIN (ITALY)

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This paper deals with the characterization of clays in soil profiles of the basin of the Trebbia river, in northwestern Italy. The profiles were described and analysed to be illustrated at the field trip of the National Congress of Soil Science (8-10 June 2002) in Piacenza (Italy).

Four profiles were studied: A1 (Mezzano Scotti) near a river terrace, B1 and B2 (Barberino) in a typical ophiolytic emergence, and C1 (S.Salvatore) inside the Bobbio Window, an important geological formation studied from the beginning of this century. The classification of soil profiles was done according to the Soil Taxonomy (1999).

Samples were collected between 2 September-5 November 2001. Soils were air-dried and on the fine earth chemical-physical analyses were carried out according National Official Methods for Soil Analysis (1999). From soils the clay fraction (<2μm) was separated by centrifugation and diffractograms were obtained of the oriented sample. For the identification of phyllosilicates the analysis was carried out on an Mg- or K-saturated air-dried sample, after solvation with ethylen glycol, and after heating at 500°C. The semiquantitative estimation of phyllosilicates was done by considering the height of the peaks.

A1 is a Typic Haplustept, fine-loamy, mixed, mesic (5 horizons) which shows scarce evolution and the presence of carbonates. This could mean that clay minerals are inherited from the parent rock,. Notwithstanding data of pH, base saturation and the parameters of drainage suggest an evolution of illite towards smectite.

B1 is a Udic Ustorthent loamy-skeletal, magnesic, mesic (5 horizons) in which the presence of serpentine and smectite was always observed, thus strengthening the autochthon origin of the soil. In general smectite evolves from serpentine under conditions of scarse drainage; this seems to be supported by textural and water retention data. Smectite can also evolve from serpentine by an intermediate step to low-charge vermiculite and in the presence of an increase of base content (Ca, Mg) in the soil. This hypothesis seems to be discarded in that the mineralogical analysis does not reveal the presence of vermiculite. In the surface horizon kaolinite and illite of possible external origin are present. The horizon at 50-64 cm depth shows too high carbonate (Ca) content, likely due to an occurrence of a calcareous breccia during the soil formation.

B2 is a Lithic Ustorthent loamy-skeletal, magnesic, mesic (3 horizons) typical of a serpentine area with the presence of serpentine and smectite suggesting the autochthon origin of the soil.

C1 is an Inceptic Hapludalf coarse-silty, mixed, mesic (5 horizons). The mineralogical composition of the profile, together with soil reaction and the saturation of the exchange complex points out the evolution of illite to chlorite (likely trioctahedral) and the weathering of kaolinite in the top horizons.

EMANATION THERMAL ANALYSIS STUDY OF CLAY MINERALS

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Emanation thermal analysis (ETA)[1,2] based on the measurement of the release of radon from minerals samples previously labeled by radium and thorium as radon parent radionuclides, has been used to characterize the microstructure changes of the samples on heating at the controlled heating rate and controlled gas environment. Changes in surface area and near surface structure irregularities, serving as channels for radon diffusion in the solids, were characterized by ETA.

The ETA results, characterizing the thermal behavior of different smectite clays, such as beidelite, saponite, hectorite and montmorillonite saturated with various cations as well as hydroxyl aluminium pillared montmorillonite, will be presented in comparison with the results of differential thermal analysis and thermogravimetry.

The ETA results of natural and chemically modified vermiculite will be presented in comparison with the results of the mathematical modeling used for the evaluation of the microstructure changes due to the release of water and other volatiles.
The possibilities of the ETA use in the characterization other clay minerals, such as goethite, hydrargillite etc. will be demonstrated.

Acknowledgment.

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MINERALOGICAL AND GRAIN SIZE COMPOSITION OF CLAYS DEVELOPING *CALANCHI* AND *BIANCANE* EROSIONAL LANDFORMS

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Clayey terrains outcropping in many parts of Italy are frequently affected by accelerated erosion processes producing landforms known as *calanchi* and *biancane*. The *calanchi* are intensely dissected landscapes, presenting rill and gully landforms and a dense dendritic drainage network. The *biancane* are landforms characterized by bare cones and hummocks, separated by flatter areas of surface wash deposits. In spite of an extensive research, the genetic processes differentiating *calanchi* and *biancane* are still poorly understood. The present study was undertaken with the aim to extend the collection of data on the properties of their parent material and to possibly establish which property plays an important role in their differentiation. Research has focused on the *calanchi* and *biancane* of Tuscany, which has a widespread occurrence of these landforms and where most of the earlier studies have been conducted. In this region, *calanchi* and *biancane* are generally developed in the clays of the Neo-autochtonous Complex, particularly in the fine-grained Pliocene sediments, which were deposited in tectonic depressions developed after the emplacement of the allochtonous Ligurian and Tuscan nappes.

Among the Neogene tectonic depressions recognized by geologists, Volterra and Siena basins may be regarded as two of the most important, both for their extension and for the thickness of their Neo-autochtonous deposits. Within these basins, a frequent occurrence of *calanchi* and *biancane* has been reported . This study focused on landforms developed in these two basins on Pliocene blue clays of the Piacenzian facies. In these areas, the morphological survey was followed by sampling of parent material of selected examples of *calanchi, biancane* and intermediate forms (*bialanchi*). The data collected suggest: a) *biancane* tend to develop in very fine sediments, such as silty clays with a very high clay content(65-70%); b) *calanchi* tend to occur in relatively coarser sediments, such as clayey silts and sandy clayey silts having a notable sand fraction (6-18%); c) both *biancane* and *calanchi* may develop in intermediate textures, such as silty clays and clayey silts, made up of approximately equal quantities of silt and clay; d) no strong trend in clay mineralogy can be correlated with the landforms; the swelling-phyllosilicate contents are roughly equivalent in the parent materials of *biancane* and *calanchi*; e) pore water chemistry seems to play a very important role in the development of these landforms; the *biancane* have high concentrations of sodium relative to other cations (essentially calcium and magnesium) in pore water; all the analysed *calanchi* pore waters have low concentrations of sodium relative to divalent cations.

ADSORPTION ON CALCINED BENTONITES

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The adsorption of vapours or liquids on porous materials plays an important role in several applications such as odour dimishing or herbicide formulations. Of special interest is the amount adsorbed and the remaining partial pressure of the adsorbtive in the gas phase or bulk concentration according to the pore volume and the specific surface area.

Thus, the aim is to focus on a cheap and easyly produceable material with acceptable adsorption properties and the possibility of recycling the porous material. Due to these requirements clay minerals show the desired properties. The texture of clay minerals can be influenced by calcination to obtain materials with differing porosities and specific surface areas.

Pure spray dried montmorillonite shows almost no accessible surface area in nitrogen adsorption experiments due to the closed structure of the clay mineral lamellea. Calcination at temperatures below 500 °C causes an evaporation of interlayer water and, thus, a new orientation of the cristallites increasing the specific surface area. Also formation of thicker stacks of lammellae with resulting macropores in the matrix leads to an increasing accessibility to nitrogen during the adsorption.

Desorption of chemically bound octaedrical sheet water above 500 °C causes additional porosity until increasing calcination temperatures above 600 °C form voluminous stacks and finally lead to a collapsed system with no accessible surface area caused by sintering processes.

For comparison of the specific surface area from nitrogen adsorption isotherms, the real accessibility of the surface and the pores was tested by the adsorption of alcohols and further organic adsorptives. The adsorption of the herbicide Sulfentrazone from aqueous solution leads to comparible results.

CLAY REINFORCEMENT OF ELASTOMERIC MATERIALS

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Addition of an inorganic component to polymers leads to improvements in various physical and mechanical properties. These improvements are the result of a complex interplay between the properties of the individual constituent phases : the polymer, the filler and the interfacial region. Filler morphology such as the particle size, structure and aspect ratio (length / diameter ratio) have a large influence on the physical performance of the polymer composite.

Layered silicate clays have attracted a great interest owing to their intrinsically anisotropic character. Used as fillers in polymer systems, they are able to disperse into the host matrix at the nanoscale level leading to polymer nanocomposites which exhibit major improvements in various properties even at very low clay content (<10 wt%) with regard to other conventional fillers. The main idea is to disperse the clay platelets with dispersions ranging from an intercalation of the polymer chains in the galleries to a total exfoliation of nanometer-thick silicate layers dispersed in the polymeric matrix thus offering a very large polymer / filler interface.

While organoclays have been largely used in various thermoplastics, a very small number of studies are reported on the use of organically–modified layered silicates to reinforce elastomers. Elastomeric materials are usually reinforced with carbon black or silica. One parameter which limits the filler capability is the filler agglomeration. Direct inter-particle contacts are important in a highly polar filler such as silica. The interlayer expansion of organoclays which leads to increased surface-to-volume ratios, would be highly desirable for a better use of the filler reinforcing capability.

This paper will report investigations carried out on elastomers loaded with organically-modified montmorillonites. The morphology of the clays was characterized by scanning and transmission electron microscopies, the interlayer spacings were determined by small angle X-ray scattering. In addition to mechanical and swelling measurements, Fourier-transform infrared dichroism and birefringence were used to analyze the orientational properties of the different networks.

ANALYIS OF THE RELATIONSHIP BETWEEN KAOLINITE AND PAPER COATING STRUCTURE AND SURFACE PROPERTIES

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Coated papers are a sophisticated paper product that has a surface with special qualities, namely in terms of sheet and print gloss, as well as printability. Kaolin is a traditional pigment for coating and, in recent years, its market share has been eroded by others pigments namely ground and precipitated calcium carbonate. There is a lot of research to be done in several fields, specially in what concerns the relationships between rheological properties of coating colors and paper coating properties, namely structure and surface.

In this research, we intend to analyse the influence of particle size on those properties. Two kaolins were selected, one with 100%<4 m (K4) and the other with 100%<2 m (K2). They have different particle size distributions and specific surface areas as well as different particle shape factors. Coating colors were characterized in terms of rheology. The coating colors formulations were based on kaolin to which 10 parts of carboxylated styrene-butadiene latex and 1 part of acrosol were added. The coating colors were coated on a base paper having a grammage of 100 g/m^2 and the coat weight aim for one side of the base paper were 5 g/m^2 for kaolin K4 and 2 g/m^2 for kaolin K2 and, finally, they were calendered. The Endupap-Universal Coating Machine was used to perform paper coating. The paper properties were: bulk, roughness, light scattering, sheet gloss, burst strength, stiffness, print gloss and ink penetration index. Surface characteristics were also evaluated with a perfilometry and with SEM observations and structure properties was evaluated with intrusion mercury porosimetry. The relationships between particle size as well as CMC molecular weigth and concentration on rheology and how these aspects influence paper coating properties were analyzed. Intrusion mercury porosimetry proved to be very sensitive relatively to particle packing and SEM, AFM observations as well as Raman Spectroscopy and perfilometry were very effective on surface analysis. Finally, assumptions about the influence of particle size of kaolins on coating properties were assessed.

MODIFIED LAYERED MINERALS FOR ENVIRONMENTAL AND AGRONOMICAL USES

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The layered structure of natural clays and the so-called anionic clays have an interlayer surface that in some cases is very large and easily modifiable and hence may retain pollutants and agrochemicals. Results of anionic clays for removing organic contaminants of anionic or polar character and organic clays as support for slow release formulation of highly mobile herbicides are presented.

The anionic clays or layered double hydroxide (LDH) can adsorb anionic organic contaminants by ion exchange, and when calcined at 500ºC, losses the layered structure becoming a double mixed oxide (DMO), which can revert in the pesence of water and anionic species the layered structure of LDH. That reconstruction mechanism is a potential via to remove anionic contaminants from water, with the additional attractiveness of its possible recyclability. The adsorption of dodecylbenzil sulphonate (DBS), 2,4,6-trinitrophenol (TNP) and 2,4,6-triclorophenol (TCP) on Mg3Al (OH)8Cl 4H2O (LDH) and its corresponding Mg-Al mixed oxide (DMO) are studied. The adsorption of polar herbicides on OLDH is shown. The adorption of the organic molecules reported are depending mainly on the properties of the contaminant and the original interlayer anion. Langmuir and Freunlich equations were applied to describe and quantify the sorption process. XRD and FT-IR techniques were used for solids characterization.

Organic clays (OCl) normally interact with polar organic compound enhancing hydrophobic partition with some polar contributions. Organocly-pesticide interaction could be considered to prepare slow-release formulation of those agrochemicals to minimize their environmental impact, such as transport to surface and ground waters. Two highly soluble water soluble and mobile herbicides, hexazinone and dicamba, were selected and their adsorp`tion on diverse OCl reported to range 50 –300 µmol/g. High layer charge clay and large hydrophobic alkylammonium favore the herbicide adsorption, despite their high water solubility and their different acid-base character. Two OCls were selected and two different herbicide-organoclay preparations tested for mobility and weed efficacy in lab and field studies. Leaching losses of herbicide could be decreased from 100 to 50% by mixing through different ways with OCl. Bioassays and field experiments show that some herbicide-Ocl preparations display the same weed efficiency as the technical herbicide . After the results obtained in this study it is demonstrated that organoclay can act as efficient support for controlled release formulations of pesticides.

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INTERACTIONS BETWEEN COLLOIDAL COMPONENTS AS AFFECTING HEAVY METAL RETENTION IN SOIL

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The fate of heavy metals in the environment is largely controlled by sorption reactions with soil colloids. Because interactions between soil constituents can significantly alter the amount and nature of the surface exposed by soil colloids for contaminant sorption, predictions of the extent of sorption based on the sum of the sorption capacity of individual soil constituents may result in serious deviation from the reality (1). Little information, exists on the interactions of contaminants with polyphasic sorbents, although in the last decade increased attention has been given to studying the behaviour of multicomponent model sorbents in order to achieve a more realistic interpretation of the sorption process in soil (2).

In the present work, the sorption capacity of binary and ternary model colloids containing montmorillonite (SW), ferrihydrite (Fh) and humic acid (HA) for two heavy metal ions [Pb(II) and Hg(II)] has been determined and compared with that of the individual constituents. The model particles were prepared in the laboratory and characterised by elemental analysis, Fourier-transform infrared spectroscopy, X-ray diffraction and specific surface area measurements. Sorption-desorption of Pb(II) and Hg(II) by the different sorbents was studied by the batch equilibration technique. X-ray diffraction and Fourier-transform infrared spectroscopy techniques were also used to assess interaction mechanisms.

For single sorbents, Pb(II) sorption was high on humic acid, moderate on montmorillonite and zero on ferrihydrite, whereas Hg(II) sorption increased in the order: humic acid >> ferrihydrite > montmorillonite. In binary sorbents, ferrihydrite coatings on montmorillonite had little effect on Pb(II) and Hg(II) sorption by the clay. Humic acid coatings on montmorillonite significantly enhanced sorption of both heavy metals, whereas humic acid coatings on ferrihydrite did not enhance heavy metal sorption. This was attributed to blockage of the functional groups of humic acid responsible for heavy metal sorption (such as carboxylic groups) as a result of their interaction with the ferrihydrite surface. A similar behaviour was observed for Pb(II) in ternary samples, but not for Hg(II), indicating that groups with different affinity/accessibility were involved in the retention of Hg(II) and Pb(II). Sorption by the model associations studied were highly reversible.

The results of this study confirmed that mutual interactions between colloidal soil constituents can greatly alter the sorption behaviour of natural particles towards heavy metal ions and that sorption predictions based on soil composition would be greatly improved with a better understanding of how these interactions affect the sorption behaviour of naturally-occurring soil colloids.

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INTERPRETATION OF Fe^{2+} QUADRUPOLE DOUBLETS IN MÖSSBAUER SPECTRA OF TRANS-VACANT MICACEOUS MINERALS

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Interpretation of Fe^{2+} quadrupole doublets in Mössbauer spectra of dioctahedral trans-vacant micaceous minerals, in spite of the main valence contribution, q_{val}, to the electric field gradient (EFG) at Fe^{2+} cations, should be based on the same common principles as for Fe^{3+} doublets, that is, on preliminary knowledge of cation distribution (CD) in the unit cell and on the local probe nature of Mössbauer spectroscopy. This means that each of j fitted doublets can be considered as superposition of certain individual i doublets corresponding to Fe^{2+} in certain local cationic arrangements within a trans-vacant octahedral sheet. These arrangements are composed of isomorphous cations (Mg, Al, Fe^{3+}, Fe^{2+}) and consist of three octahedral cations nearest to the central Fe^{2+}.

The most important components of the approach developed for interpretation of Fe^{3+}-doublets [e.g. 1, 2] are the individual quadrupole splittings Δ_i for Fe^{3+} in possible local cationic arrangements, and computer simulation of two-dimensional CD using the IR data in the region of OH stretching vibration [3] as the basic parameters. As the CD simulation yields, in particular, the occurrence probabilities for Fe^{3+} in different local cationic arrangements, the aim of a Mössbauer spectrum interpretation is the CD reconstruction that would satisfy both relative areas S_j and Δ_j for the fitted doublets.

Using this approach, CD-reconstructions for a representative collection of celadonite, glauconites and ferriillites were obtained. The improved CD simulation program made it possible to manipulate with Fe^{2+} and to analyze the local cationic arrangements around Fe^{2+} in the same way as for Fe^{3+}.

The CD reconstructions obtained with respect to Fe^{3+} and its contribution to Mössbauer spectra were analyzed to find initial dependence of Δ_j values for Fe^{2+} on the compositions of the local arrangements and their occurrence probabilities. Then, the initial dependence was defined more precisely using the potentialities of CD simulation program. The correlations between quadupole splittings Δ_j fitted to the spectra and chemical composition of the studied samples and between Δ_j values and composition of local cationic arrangements around Fe^{2+} yield a number tentative individual Δ_i^{tent} values for Fe^{2+} :

Arrangement	Δ_i^{tent} (mm/s)	Arrangement	Δ_i^{tent} (mm/s)
$3Fe^{3+}$	1.61	$2AlFe^{3+}$	2.49
$2MgFe^{2+}$	1.65	3Al	2.85
$2Fe^{3+}Al$	1.92	2MgAl	2.85
3Mg	1.96	2AlMg	2.96

Thus the CD reconstructions satisfying Mössbauer spectra can be controlled now not only by Fe^{3+} but also by Fe^{2+} cations.

The Δ_i^{tent} values found for Fe^{2+} imply the direct dependence of quadrupole splitting Fe^{2+} on the distortion of Fe^{2+}-site: the more the distortion (described as a competitive influence of a charge and size heterogeneity in nearest neighbouring octahedra) the more the quadrupole splitting Fe^{2+}.

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DIOCTAHEDRAL LAYER-SILICATE INITIATION AT 90°C IN ALUMINOSILICATE GELS WITH Si:Al RATIOS NEAR UNITY

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Although halloysites clearly form in soils under ambient conditions, they have never been synthesized in the laboratory from allophanic precipitates. Wada et al.(1) and Farmer et al.(2) have shown that an incipient layer-silicate does form when freshly precipitated allophanes with Al:Si ratios 1.08-1.5 are digested at 80-100°C at pH 8-9. Their composition suggests that the products might have a halloysite component.

In order to obtain a better organized product we have extended digestion times to over 52 weeks, and compared the effects of different cations on the product.

Using Na_2CO_3, K_2CO_3 or $CaCO_3$ as the alkaline agent had no significant effect on the product, although Ca tended to stabilize the hydrous feldspathoid structure of the initial precipitate. The best-organized products had all the characteristic IR features of a dioctahedral clay, with an OH stretching band at 3615-3627 cm^{-1} and two OH bending features at 900 and 935 cm^{-1}. This indicates two distinct structures in the product, one halloysite-like with an OH bend at 935 cm^{-1}, which is lost on heating the clay to 300°C, and the other beidellite-like with an OH bend at 900 cm^{-1}, which survives in part to 500°C.

X-ray diffraction showed the typical *hk* bands of a layer silicate, but no basal reflections in the 0.7- 1.5 nm range, although a broad feature at 0.37 nm shifted to 0.39 nm on treatment with glycol. High-spacing fringes near 4.1 nm, 2.7 nm and 2.0 nm suggest a degree of regularity in particle size and structure.

High-resolution electron microscopy showed spheres of 13-30 nm diameter, which exhibit a remarkable reticulated internal structure, suggesting layers, irregular in structure, of short extent, and sometimes changing direction.

We believe that the product includes Al hydroxide, halloysitic and beidellitic layers in random arrays with too little regularity in the stacking to give a basal reflection, but with interlayer spacings that share a higher order of 0.39 nm when glycollated.

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SORPTION OF TRICYCLAZOLE AND METALAXYL ON A SOIL CLAY: EFFECT OF ORGANIC MATTER REMOVAL

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Organic matter has been considered the primary adsorbent for pesticides[1], although many studies also reveal the relevance of mineral surfaces in sorption, specially below a certain organic carbon level and in the case of polar compounds[2]. The soil clay fraction as a whole (mineral and organic components) has been shown to be responsible for the sorption of many polar pesticides[3]. In soil, clay and organic components are usually intimately associated such that their individual effects on sorption are difficult to separate. The importance of the different components of soil on pesticide sorption is generally evaluated by determining the sorption behaviour on selected soils and in some cases, by investigating changes in sorption after removing soil components. The aim of our study was to assess the influence of peroxidation on adsorption of the fungicides tricyclazole and metalaxyl, of different water solubility (1.6 and 7 g/L, respectively) on a soil clay from a saline soil from marshes of Southern Spain, which has been shown to be highly effective in sorption of polar herbicides[4]. The colloidal fraction of the soil (soil clay) was obtained by sedimentation using the pipette method with previous carbonate elimination. The soil clay was treated with 30 % hydrogen peroxide for removal of organic matter and then washed with 0.5 mol/L $CaCl_2$ and freeze-dried. Physicochemical properties of the soil clay, before and after peroxidation, were determined following the usual lab methodology, and clay mineralogy by X-ray diffraction procedure on oriented specimen (Table 1)

Table 1. Clay mineralogy (illite, kaolinite, montmorillonite), physicochemical properties of the natural soil clay and soil clay after peroxidation and distribution coefficients Kd calculated at 20 µM equilibrium concentration (µmol sorbed kg^{-1}soil/µmol L^{-1}in solution).

Soil Clay	Clay Mineralogy %			pH	OC %	CEC Meq/100g	S_{BET} m^2/g	Tricyclazole Kd	Metalaxyl Kd
	I	K	M						
Natural	37	11	16	7	0.54	45	0.104	11.2 ± 1.2	2.9 ± 0.77
After H_2O_2	37	11	16	6.9	0.12	27	0.138	13.5 ± 0.81	57 ± 1.5

The amounts of tricyclazole or metalaxyl sorbed to the soil clay were calculated by shaking 0.5 g of clay with 10 mL of a 20 µM solution of tricyclazole or metalaxyl for 24 h. Suspensions were then centrifuged and equilibrium concentrations determined in the supernatants by HPLC. A distribution coefficiente K_d (fungicide sorbed/fungicide in solution) was calculated and given in Table 1. Tricyclazole adsorbs on soil clay to a much higher extent than metalaxyl, and there is only a small increase in sorption after H_2O_2 treatment. On the contrary, metalaxyl sorption highly increases when organic matter of the soil clay is reduced from 0.54 to 0.12. The high increase in S_{BET} is probably the reason for the high increase in sorption of metalaxyl upon H_2O_2 treatment. Interactions between clay and organic matter reduces the availability of surfaces to pesticide sorption, and elimination of organic matter associated to the mineral surface of the clay fraction increases available surface for sorption, revealing the important role of the mineral surfaces in sorption of the highly water soluble metalaxyl.

Acknowledgements

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CATALYTIC WET PEROXIDE OXIDATION OF PHENOL OVER PILLARED CLAYS CONTAINING IRON SPECIES

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Although wet oxidation is not a new technology, considerable improvements have been proposed and performed in the last 10 years in order to oxidize organic pollutants into carbon dioxide or into products which are able to be eliminated by biological treatment.

The catalytic wet peroxide oxidation (CWPO) appears to be potentially a more efficient process than the catalytic wet air oxidation (CWAO) since the oxidizing properties of hydrogen peroxide are stronger than those of molecular oxygen allowing to perform the reaction at conditions close to the ambient ones.

Among the different catalysts able to fully oxidized phenol or its substituted forms, only few of them show a significant catalytic activity and stability in aqueous media.

Due to their low cost and high efficiency, the clay-based catalyst appears to be very attractive. We have chosen to study the catalytic phenol (as model molecule) oxidation with hydrogen peroxide over an iron containing (Fe=3.04 wt%) pillared clay.

The reaction was performed in a semi-batch reactor, at pH=3.7, with a continuous addition of the hydrogen peroxide solution, so that the stoichiometric excess of the hydrogen peroxide was only 1.14 after 4 hours of reaction. At 70°C, the TOC abatement was close to 80%, with a total phenol conversion. A very low iron leaching was observed since after more than 350 hrs of use in a continuous flow reactor, less than 3% of the initial iron content (Fe=3.01 wt%) has been lost.

The characterization of the fresh and used catalysts by ESR spectroscopy (see Fig.) has shown that the iron is present as isolated species and oxide clusters. The isolated species are likely located on the clay framework and associated to the alumina pillars as substituting cation or extra species. After a long reaction time, only the ESR signal assigned to the smallest oxide clusters is modified whereas the catalytic activity remains constant suggesting that the iron active species are the isolated ones.

By using a spin-trapping technique, the ESR experiments showed that the reaction proceeds mainly from HO° formation without significant formation of electrophilic oxygen species.

The high stability of that pillared clay catalyst in the reaction conditions and its high efficiency towards the phenol elimination without excessive hydrogen peroxide consumption allows to use it in a continuous process of organic pollutants elimination in water.

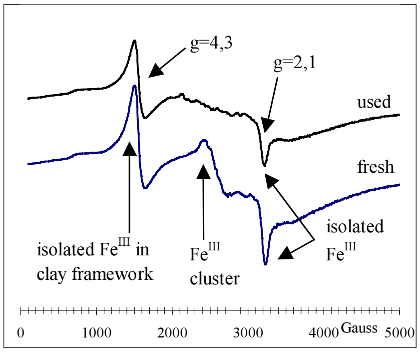

Figure : ESR Spectra of the catalysts at 77K under vacuum (10^{-4} Torr), Frequency : 9.25 MHz.

COLLOIDAL LAYERED DOUBLE HYDROXIDES AND HETEROCOAGULATION WITH MONTMORILLONITE

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Colloidal magnesium aluminum hydroxide, the most important layered double hydroxide, was obtained by peptization of crystalline materials by intense washing. We determined the electrophoretic mobility of the particles, the critical coagulation concentrations, and the flow behavior of the dispersions.

The hydroxide dispersions were completely coagulated by sodium montmorillonite when the montmorillonite mass fraction was ≥ 0.06. The sodium montmorillonite dispersions required a magnesium aluminum hydroxide mass fraction of ≥ 0.2. The heterocoagulates thus formed at hydroxide mass fractions $0.2 < \chi < 0.94$ showed a maximum yield value at $\chi \sim 0.4$ due to the formation of extended stable networks composed of the differently charged particles. A maximum value of the specific surface area was reached at higher hydroxide fractions, $\chi \sim 0.65$.

The strong influence of the heterocoagulation on the flow behavior, the specific surface area and the porosity provides a simple method to optimize the properties of colloidal bentonite dispersions in practical uses.

DISTRIBUTION OF WATER LAYERS IN DEHYDROXYLATED-REHYDROXYLATED SMECTITES

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Three samples (Wyoming and Camp Bertaux montmorillonites, Unterrupsroth beidellite) differing by the localization of the deficit of charge have been studied. Wyoming montmorillonite sample has been exchanged with different interlayer cations. These samples are constituted of *cv* layers (*cv* for vacant octahedral sites in *cis* positions). Dehydroxylation treatment consisting by heating from room temperature to 750°C for montmorillonites and 650°C for the beidellite have been applied. These are accompanied by a migration of the octahedral cations from former *trans*-octahedra to empty *cis*-sites [1]. To rehydroxylate samples, gold capsules have been filled with 15 wt.% water and placed in a Tuttle-type pressure vessel at 350°C (300°C for the beidellite sample), 1 kbar PH_2O during 5 days.

The nature (*cv* or *tv*) of the layers in the natural (N) and rehydroxylated (R) states has been determined using thermal gravimetric analysis [2].

In smectite clay minerals, the relative weakness of the bonding between layers, through the interlamellar cation (Na, Ca…), allows the intercalation of water molecules (which are disposed in layers) in the interlayer space. To characterize the distribution of water layers in N and R materials, SAXS (Small Angle X-ray scattering) analysis have been investigated. The experimental patterns shown a increasing of the width of the modulation in the R specimens in comparison to the N ones. The apparent interlayer distances $d_{ap}(\AA)$, before and after the dehydroxylation-rehydroxylation cycle, are very similar.

The value of the structural parameters; $\overline{d}(\AA)$ (mean interlayer distance), $\overline{M}$ (mean number of stacking layers) and disorder, determined by adjusting the theoretical spectra to the experimental ones are given in the following table.

		Interlayer hydration				Structural parameter			
		w_{0C}	w_{1C}	w_{2C}	w_{3C}	$\overline{d}(\AA)$	$d_{ap}(\AA)$	$\overline{M}$	Disorder
Wyoming-Na	N	0.35	0.49	0.16		12.1	12.2	200	0.024
Wyoming-Na	R	0.55	0.18	0.27		11.9	12.9	200	0.040
Wyoming-Ca	N		0.25	0.56	0.19	15.3	15.4	170	0.017
Wyoming-Ca	R		0.44	0.24	0.32	15.1	15.7	200	0.030
Camp Bertaux-Na	N	0.47	0.24	0.29		12.1	13.1	80	0.034
Camp Bertaux-Na	R	0.48	0.13	0.39		12.4	13.8	40	0.039
Unterrupsroth-Na	N	0.17	0.71	0.12		12.4	12.3	45	0.014
Unterrupsroth-Na	R	0.28	0.58	0.14		12.2	12.2	130	0.020

The results shown that the water layers distribution is modified after the dehydroxylation-rehydroxylation cycle. For all the samples, an increasing of the disorder parameter characterize the treatment effect (see table). For Na samples, the disorder parameter decreases with the proportion of tetrahedral charges in the N and R state and the number of layers with zero water layer increases after the cycle. For the Wyoming-Ca sample, there are not zero water layer and it is the number of layers with one water layer which increases. This study shows that, in smectite particles, the distribution of water layers is connected to the localization of the deficit of charge and to the nature of the interlayer cation.

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GEOLOGICAL, MINERALOGICAL AND PETROGRAPHIC INVESTIGATION OF YUKARIKARAÇAY (HONAZ) DOLOMITIC CLAYS IN DENIZLI REGION (SOUTHWESTERN ANATOLIA TURKEY)

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The study area covers Yukarıkaraçay (Honaz) district and its surrounding area in the Denizli region. The rock sequence commences at the base with the Upper Cretaceous-Paleocene autochthonous plysch overlain by a neritic limestone of the Mesozoic and by an ophiolitic series with tectonic contacts in the investigated area. All of these formations are overlain by fluvial and lacustrine sediments of the Late Miocene-Lower Pliocene.Neogene sedimentary sequence that commences at the base with red claystone and sandstone and continues upwards alternation marl, clayey conglomerate-sandstone and limestone. Kocapınar (Denizli) volcanics are mainly composed of basaltic lavas and tuffits. Basalt and synsedimentary vitric tuffs cut and drag dolomitic claystone. The age of Denizli lavas have been obtained and ranged from 6.00 to 4.88 Ma using the $^{40}Ar^{39}$ age method (Paton, 1992). In the thin tuffit layers within the dolomitic claystone are found dolomite and claystone pebbles. Shoshonitic basalt, latite and trachyte lavas outcrops indicate the last presence phase of volcanism.

Claystone specimens were examined by XRD, DTA and SEM. They contain mostly smectite, illite, montmorillonite and palygorskite. In the claystone, the average of sandy and silty particles larger than 0.074 mm are 4.85%**.** Silt and sand size particles are comprised of dolomite, calcite quartz and albite. The average of chemical analyses of red and brown color clay specimens with particles smaller than 0.074 mm are SiO_2: 44.74%, Al_2O_3: 7.5 %, Fe_2O_3: 7.95 %, CaO: 9.11%, MgO: 10.7 %, SO3: 0. 07 %, Na_2O: 0. 22 %, K_2O: 1.14 % and LOI: 16.67%. In addition, the average chemical analyses of white color clay specimens with particles smaller than 0.074 mm are SiO_2: 32.44 %, Al_2O_3: 2.86 %, Fe_2O_3: 5.67 %, CaO: 16.92%, MgO: 15.51 %, SO_3: 0. 064 %, Na_2O: 0. 23 %, K_2O: 0.20 % and LOI: 25.197 %.

The average liquid (LL), plastic (PL) and shrinkage limit (RL) of red and brown color clay specimens are 72, 52, 20.11 and the average of liquid (LL), plastic limit (PL) and shrinkage limit (RL) of white color clay specimens are 74.8, 50.2, 17.50. The average unit weights of red color clay and white color clay are 2.43 grf/cm^3 and 2.40 grf/cm^3 and the values of water absorption as volume and weights on the clays are determined. For red color clays, the values of water absorption as volume and weight are 63.0 %, 38.43 % and for the white color clays are 69.25 % and 46.62 %, respectively. According to laboratory tests, soil classification was defined as MH (plastic clay) according to the USCS soil classification system. White clays are in the active clay class. Red color clays are normal clay in regard to activity.

According to Akbulut and Kadir (2001), some volcanic springs in the basin gushed out and formed oncolitic algal accumulations. Since the spring water was rich in iron, the synsedimentary material was red colored due to the oxidation. Sepiolite precipitated in local platy hollows at the bottom of the lake where Mg and Si contents and pH were high. However, formation of palygorskite and smectite was controlled by Al concentration and pH. Thus, in an environment with higher Al and pH smectite, and relatively lower Al and pH palygorskite were formed.

PETROGRAPHICAL AND PETROCHEMICAL INVESTIGATION OF SANDIKLI CHABAZITIC AND PHILLISITIC TUFFS AND THEIR USAGES AS BUILDING STONE AND LIGHTWEIGHT AGGREGATE CONCRETE (WESTERN ANATOLIA, IN TURKEY)

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In the study area, the Middle-Upper Miocene aged trachyandesitic, andesitic and phonolitic lavas, tuffs and tuftits are formed. Tuffs are mainly vitritic and vitritic-crystal tuffs. Tuffs have various ratio pyroclast, extraclast, pyrogenetic and secondary minerals. In the tuffs, pyroclasts have microlitic and micro-porphyric texture and they contain albite, sanidine, honblende, augite and opaque minerals. Extraclasts (volcanic and non volcanic) are found various sizes and amounts in tuffs. Augite, hornblende and biotite were observed as pyrogenetic minerals in matrix. There is shapeless emptiness in glassy matrix that has intense zeolitization. Crème tuffs contain chabazite and/or chabazite and phillipsite. Milky brown tuffs contain phillisite. Phillipsitic tuffs are more welded and have fewer voids than the chabazitic tuffs. In the glassy matrix of chabazitic tuffs are much the transforming to the clay (illite, montmorillonite) than the phillipsitic tuffs. Zeolite contents of tuffs were determined between 35-65%.

For the usage of building stone, physico-mechanics properties of tuffs, such as bulk density, specific gravity, apparent porosity, as weight and volume absorption and compressive strength were determined and are 1.367-1.856, 1.77 gr_f/cm^3-2.01gr_f/cm^3, 27.4 %-32.3%, 13.40%-24.45% and 57.81 kg_f/cm^2-294.92 kg_f/cm^2, respectively. When the bulk density, specific gravity, and water absorptions of tuffs increase, the compressive strength of tuffs increased. Although the values of apparent porosity decreased, the compressive strength of tuffs decreased. As a result, physico-mechanical properties of phillipsitic tuffs are better than the chabazitic tuffs and the milky brown welded tuffs that have shown high strengths. They can be used as a building stone without any processing. On the other hand, the crème color tuffs having low specific gravity and low strengths may be used naturally as light building stone and insulation material.

In addition, in this study the effect of the zeolite minerals within the zeolitic tuffs on the strength of concrete was investigated by producing concretes with lightweight aggregates. We made BS16 type concrete (the assumption of a certain minimum strength of concrete is 160 kg_f/cm^2) from the aggregates of crushed tuffs, having maximum sizes of 4 mm and 8 mm. The average cylinder strengths of the concretes are 167.7 kg_f/cm^2 and 160.7 kg_f/cm^2, for the 4 and 8 mm aggregates, respectively. High strengths were determined with milky brown welded tuffs, which contain high zeolite concentrations. High zeolite contents in the tuffs cause an increase in the concrete strengths. It is concluded that milky brown welded tuffs in the study area can be used in the construction sector.

ADSORPTION OF METOLACHLOR ON MESOPOROUS SILICA AND ORGANICALLY FUNCTIONALIZED POROUS SILICA

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Since the discovery of MCM-41 in 1992, many workgroups focused their research on mesoporous materials. The high surface area and the uniform pore size, with a pore diameter, which can be tailored by a liquid-crystall templating mechanism, are the interesting properties of these materials. We investigated the adsorption properties of meso- and microporous silica in order to find slow-release formulations of herbicides with reduced leaching.

We synthesized and characterized micro- and mesoporous silicas. The used hydrated sodium silica solution or tetraethoxysilane as silica source, different cationic surfactants and different pH-values for the synthesis. To remove the surfactant, different calcination temperatures or extraction with ethanol were used. The materials were characterized with nitrogenadsorption-isotherms and X-ray. To increase the hydrophobicity of the porous silica, we modified the surface with chlorotrimethylsilane. Additionally, we synthesized an organically functionalized mesoporous silia with an organosiloxane precursor. Metolachlor adsorption isotherms on porous silica were measured by batch experiments at solid contents of 2.5 g/l.

The amounts adsorbed of metolachlor on the mesoporous silica with surface areas of 600 – 700 m^2/g and pore diameters between 1.0 – 3.0 nm are in the range of 10 – 15% of the added amount of the herbicide. Only the material with the pore diameter of 1.6 nm and the same surface area adsorbed 37%. Including van-der-Waals radii the longest diameter of the metolachlor molecule is 1.14 nm. Due to this geometrical fit the adsorption potential of metolachlor in pores with a diameter of 1.6 nm is higher. Nevertheless the type of the adsorption isotherm revealed that the hydrophilic silica surface is not the best adsorbent for the oily herbicide. Materials with higher surface areas (1100 m^2/g) adsorbed more (45%), but only if the pores are large enough. A microporous materials with a surface area of 1500 m^2/g only adsorbed 20% of the added amount of the herbicide. Probably the pore diameters are too small.

The surface modification with chlorotrimethylsilane increased the adsorption from 15% to 45%. The reaction of chlorotrimethylsilane with the silanol groups of the silica surface increased the hydrophobicity and reduced the pore radius.

Organically functionalized porous silica was prepared with tetraethoxysilane and phenyltriethoxysilane. We received a hybrid inorganic-organic material with phenyl functionalized pores of 1.8 nm pore diameter. This material adsorbed nearly the whole amount (more than 95%) of metolachlor in an aqueous solution. Thus, we propose that the aromatic interactions (π-π-interactions) are important for the adsorption mechanism of metolachlor. The phenyl functionalized porous silica will be tested for slow-release formulations.

CLAY–LIPOSOME FORMULATIONS OF SULFOMETURON YIELD REDUCED HERBICIDE LEACHING

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Herbicide mobility in soils has long been of concern for many reasons, including (1): (i) potential to contaminate groundwater; (ii) reduction in efficacy when herbicide is leached below the weed seed zone, which can potentially injure the treated crop; (iii) potential to return to the soil surface to injure subsequent crops. The controlled release formulations of herbicides (CRFs) provide a slow release of the active ingredient at an adequate rate, thus reducing the amount of chemical needed for an efficient weed control. The current study demonstrates the use of liposomes as a new tool for designing controlled release formulations of sulfometuron (SFM), a sulfonylurea herbicide. The herbicide was incorporated into vesicles formed by quaternary amine cations (DDAB, DDOB), which were subsequently adsorbed on a standard montmorillonite (SWy-2).

Table 1 demonstrates the potential use of DDAB for the development of CRFs of sulfometuron, unlike the organic cation DDOB.

Table 1. Adsorption and release percentages of SFM from vesicle solutions onto montmorillonite at two clay concentrations.

Clay conc. (g/L)	Cation, conc. (mM)	SFM (mM)	SFM adsorbed (%)	SFM desorbed (%)
1.6	DDAB, 6	0.6	59.1	20.0
3.6	DDAB, 6	0.6	84.6	9.5
1.6	DDOB, 6	0.6	24.3	39.2
3.6	DDOB,6	0.6	37.0	38.3

Elution curves corresponding to the commercial formulation (OUST) and those developed for 1.6 and 3.6 g/L DDAB-montmorillonite formulations were fully symmetrical, the maximal desorbed amount of SFM occurring at 53 mm rain. The total desorption percentages of SFM were 95, 49 and 26% of the total amount applied, for the commercial, 1.6 and 3.6 g/L DDAB-clay formulations, respectively. Moreover, the amount desorbed of SFM from the formulation at 3.6 g/L is about 1.5-fold lower than that at 1.6 g/L which is in agreement with the results from Table 1 where the lowest desorbed amount was obtained for the highest clay concentration.

The DDAB-clay formulations of SFM also had a higher herbicidal activity at the top five cm of the surface, which is the more critical depth, than the commercial formulation. The DDAB formulations presented inhibition percents of 29.6 and 21.1% in contrast to the low percent of the commercial formulation (3.4%).

The combination of the results of release, leaching and herbicidal activity shows that vesicle-clay formulations of SFM is a useful alternative for reduced leaching and retaining herbicidal activity to the commercial formulation.

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A REVIEW ON THE USE OF SLIP CLAY-S FOR CERAMIC DECORATION FROM ANCIENT TIMES TO THE PRESENT

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ABSTRACT

Slip or engobe is a coating or decoration of a mixture of clays, fluxes, pigments and nonplastics that is applied on a ceramic body to form a color smoothly covering all surface defects and coarse particles.

The use of the slip has been traced to very remote ages and all stages of culture in many parts of the world. Neolithic pottery dating to about 3000 B.C. decorated with red, black and white slips has been found in Eastern Asia. Egyptian potters during the Twelfth Dynasty (2160-1788 B.C.) used slips. Pottery relics from Corinth, Greece have been decorated with designs painted there on with slip. These are attributed to a period earlier than the sixth century B.C.

Castor ware made in Britain during the Roman occupancy has a white paste body with dark-colored slip. A style of decoration known as "barbotine" is believed by Walters to have originated at an early period in Gaul or Germany.

Terra sigillata is antique pottery of Roman origin made with a vitrified red-brown glossy clay coating. The technique was developed in the eastern Mediterranean in the first century B.C. and its development spread with the Roman Empire.

In this research modern Terrasigillata techniques is investigated. The preparation of raw materials, applying techniques and firing process are studied with some examples.

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INTERPRETATION OF IR SPECTRA OF DIOCTAHEDRAL 2:1 PHYLLOSILICATES IN THE REGION OF OH STRETCHING VIBRATIONS

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Diversity of isomorphous cation substitutions in structural sites is a characteristic feature of dioctahedral smectites, micas and interstratified illite-smectites (I/S). Various spectroscopic methods (in particular, IR spectroscopy) are generally used to study the isomorphous cation distribution within the 2:1 layers. The major problem here is to ensure reliable and unambiguous interpretation of experimental spectroscopic data.

Our purpose has been to analyze the potentials in the application of IR spectroscopy in the region of OH stretching vibrations for (a) quantitative analysis of 2:1 dioctahedral phyllosilicates and (b) study of the two-dimensional octahedral cation distribution. For IR spectra of micas, an unambiguous interpretation of OH stretching frequencies was suggested previously, whereas for smectites and I/S, the problem remained unsolved because of the difficulties associated with the considerable contribution of interlayer water to the spectrum. To minimize this contribution, special experimental techniques have been developed for sample preparation and spectra recording. Using these techniques, IR spectra were recorded for a representative collection of smectites and I/S of various compositions. For each spectrum, the OH stretching vibration region was decomposed and the bands were assigned to specific types of OH-bonded cation pairs. Similarities and discrepancies between these band assignments and those known for micas were analyzed.

Our results show that IR spectra in the region of OH stretching vibrations cannot be used for quantitative determination of dioctahedral smectites, micas and I/S in their mixtures. At the same time, under favourable conditions, the overall amount of Fe could be semiquantitatively estimated. For monomineral varieties with known chemical composition, the IR data can be employed in the analysis of the two-dimensional distribution of octahedral cations.

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