ANEXOS CIENTÍFICOS de interés para futuras investigaciones.

Ceramicas De Alta Porosidad A Partir De Oxidos Metalicos, Utilizando Compuestos Volatiles De Cobre. Victoriano, Luis 94.21.01-1/Interno. Chile

Se pretende estudiar un número reducido de materiales cerámicos en que se ha generado alta porosidad por medio de complejos volátiles de cobre, formados in situ. Al mismo tiempo, y en forma separada, se pretende sintetizar y caracterizar los compuestos volátiles involucrados, para lograr una mejor comprensión de la química desarrollada.

Remocion De Contaminantes Metalicos (Hg Y Cr) Del Agua Por Carbones Activados Y Zeolitas
Departamento De Fisicoquimica. ARRIAGADA, RENAN, RUBY CID, RAFAEL GARCIA. 95.22.0771-2/Fondecyt/1995-1997.Chile

Se prepararán y modificarán carbones activados de Eucaliptus globulus y cuescos de durazno y se modificarán zeolitas sintéticas y naturales, con el fin de obtener adsorbentes y/o intercambiadores iónicos con variadas características texturales y químicas. En estos sólidos se estudiará la velocidad y capacidad de retención de los iones metálicos Hg(II), Cr(III) y Cr(VI) desde soluciones acuosas. Se espera obtener información de la influencia de las características texturales y químicas de estos sólidos en la velocidad y capacidad de retención de los iones mencionados. Estos estudios de retención se llevarán a cabo tanto en régimen estático como dinámico, evaluándose al mismo tiempo el efecto de las variables de operación: temperatura del proceso, concentración inicial de los iones metálicos, pH de las soluciones, tamaño de partícula y tiempo de contacto en la velocidad y capacidad de retención de los iones considerados en los distintos carbones activados y zeolitas obtenidas.

Obtencion De Gomas De Interes Industrial Por Modificacion Quimica De Goma Natural de Euphorbia lactiflua. Interés como estabilizante de las Tierras.
94.23.983-2/FONDECYT.Chile. GNECCO, SARA, AMALIA POOLEY, MARLENE ROECKEL

Las plantas productoras de látex y resinas, nativas de zonas áridas, constituyen una potencial fuente renovable de intermediarios químicos y combustibles. El cultivo de estas especies con fines industriales podría llegar a implementarse en Chile, debido a sus características geográfico-económicas: grandes áreas de terrenos áridos; alta radiación solar (I[[ordfeminine]] IV Regiones); baja densidad poblacional; nivel técnico adecuado; existencia de varias especies productoras de látex y resinas; necesidad de importar el 85% de los hidrocarburos consumidos y el 100% de algunas materias primas que pueden obtenerse de estas especies.

Evaluaciones químicas de diversas plantas chilenas, nos llevaron a seleccionar Euphorbia lactiflua *(el lechero) como fuente promisoria de goma; estudios posteriores de tipo biotecnológico demostraron que es posible aumentar el rendimiento de goma en esta especie por medio de inductores químicos de poliisopreno y que además se puede implementar el cultivo masivo de* E. lactiflua *por medio de cultivo de tejidos "in vitro". Para explotar esta especie comercialmente se tendrían que obtener, a partir de su látex, compuestos químicos de mayor valor agregado que la goma natural, lo que constituiría un logro de gran importancia económica, tecnológica y ecológica.*

En esta investigación se propone obtener y caracterizar diferentes polímeros de importancia industrial por medio de transformaciones químicas de la goma natural del lechero: polímeros telequélicos, gomas epoxidadas, gomas cloradas y gomas maleizadas. Además se estudiaría la variabilidad estacional del rendimiento y propiedades fisicoquímicas de la goma natural de E. lactiflua. *Los resultados permitirán seleccionar las épocas de recolección de látex más adecuadas y las condiciones de reacción óptimas para obtener polímeros que puedan ser utilizados en la industria química relativa a la goma, como sustituto de materias primas que actualmente se importan.*

HISINGERITE: THE FERRIC ANALOGUE OF SPHERICAL HALLOYSITE

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Hisingerite, first described in 1810, has been variously regarded as a septechlorite, as ferric allophane, as ferric halloysite, as non-crystalline, or as poorly crystalline nontronite. Hisingerite from the original localities of Gillinge and Riddarhyttan in Sweden, has a composition close to Fe2O3.2SiO2.nH2O. X-ray diffraction analysis of Ryddarhyttan hisingerite yields very broad maxima at 7.7Å, 4.44, 3.57, 2.56, 2.26, 1.69, and 1.54Å, and that from Gillinge is similar. Cation exchange capacities are 2.2 meq/100g (Ryddarhyttan) and zero (Gillinge). Transmission electron microscopy shows a fabric of concentric spheres and part spheres, with a diameter of about 140Å, and shell walls 7Å thick. High resolution images of the sphere walls reveal a two layer structure similar to that of kaolinite. A calculated diffraction pattern based on a 4-layer shell of ferric kaolinite structure matches the observed pattern quite closely. Some other hisingerites, notably that from from Bellevue King Mine, Idaho, shows 10-Å layers as well as 7-Å layers, and this hisingerite has a CEC of 32meq/10g and a weak 15.5-Å X-ray reflection in addition to a pattern similar to Riddarhyttan hisingerite. It is concluded that hisingerite is a spherical ferric 7-Å 1:1 layer silicate analagous to halloysite, and that many of the hisingerites reported in the literature contain admixed nontronite.

OXIDATION OF A KAOLINITIC CLAY BED IN PLEISTOCENE (?) AGE STRATA FROM COASTAL PLAIN SEDIMENTS, GEORGIA, USA

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The genesis of essentially monominerallic commercial grade deposits of kaolin in Georgia and South Carolina has long been disputed. Weathering, source material,and environment of deposition are all cited as factors contributing to their formation. Stratigraphically equivalent unweathered and oxidized kaolinitic claystones collected across a redox boundary provide an unique opportunity to observe the affects of weathering on the type of kaolinite-rich sediments that may have altered to form the commercial grade kaolins. This investigation demonstrates that weathering causes extensive post-depositional alteration of kaolinite-rich neritic muds. Samples of unweathered (gray) and oxidized (tan) clay were examined to monitor compositional and textural response to oxidative weathering both on a bulk rock and microscale basis. Depletion of Si, S, and C along with enrichment of Fe reflect leaching of silica-bearing phases such as opal-A and smectite; precipitation of goethite; dissolution of pyrite; and loss of organic matter. Also observed is coarsening of kaolinite, possibly as a result of recrystallization, and an increase in the abundance of vermiform kaolinite. Chemical and structural modification of the recrystallized kaolinite was not documented although with more intensive weathering such changes would be expected. Meta- halloysite is abundant in both samples and occurs as large single tubes or as smaller tubes rimming pseudohexagonal kaolinite plates.

CLAY MINERALS IN CONTROL OF THE REDOX ENVIRONMENT IN CLAYEY SOILS AND SEDIMENTS

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Throughout Denmark, the unconsolidated surface is composed entirely of glacial sediments. The county was covered by glaciers several times during the Pleistocene.Free of ice (13-14 Ka B.P.) the área was made up of deep unweathered, reduced deposits. Owing to post-depositional oxidation *processes, a sequence of browncolors had formed in the original unweathered greyish colored deposits. In clayey sediments (clayey till and melt-water clay) of Denmark the oxidized, weathered zone is typical down to depths of 3-6 meter. The composition of the clay minerals in the oxidized zone had changed, and a total-transformation of chlorite, illite, and illite-smectite to smectite and vermiculite was observed. The weathering processes and changes in clay mineral constituents were paralleled by changes in the clay*

properties, e.g., CEC and mineral-bound electrons. Typically, about 10 % Fe(II) of total Fe in clay minerals remain in the upper part of the oxidized zone, but about 50 % Fe(II) of total Fe was in the unweathered zone. The formation of structural Fe(III) and consequent electron transfer controls the redox environment and the fate of different pollutants. For instance below arable land, moderate to high concentrations of nitrate occurs in the oxidized clayey deposits only. Iron rich clay

minerals can undergo in situ redox cycling and the inherent pools of structural Fe(II) and electron of soils/sediments may be renewed as a result of microbial activity.

GEOLOGY AND COMPOSITION OF CLAY RAW MATERIALS FOR THE ITALIAN BRICK AND ROOFING TILE INDUSTRY

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Italian brick and roofing tile industry uses some 20 million tons per year of clay raw materials coming from various deposits differing for age, geological features,compositional and technological characteristics. These differences are illustrated taking into consideration more than 300 clay samples which were characterised by chemical, mineralogical and granulometric analyses. All the samples were classified according to their prevailing use in the manufacturing of the various typologies of bricks and roofing tiles. The major clay sources are represented by three widespread geological units: grey-blue clays (Pliocene-lower Pleistocene); fluvial-lacustrine,Holocene deposits; fluvial and fluvio-glacial deposits (middle-upper Pleistocene). All the other sources substantially have just local importance.

From the compositional viewpoint, clays can be subdivided into two main groups depending on their carbonate content. Fluvio-glacial (northern Italy) and lacustrine (Tuscany) pleistocenic clays are practically carbonate-free, while the other raw materials are more or less rich in calcite and/or dolomite (average >20%). Only the clays coming from the Sillano Formation contain intermediate amounts of carbonates; these materials are exclusively used for paving bricks (Tuscan cotto). All the raw materials are characterised by a clay minerals to quartz+feldspars ratio close to one. The clay fraction is mainly constituted by illite (mostly between 60 and 70%) and chlorite (around 20%), while the amount of smectite is variable up to 40%. From a granulometric point of view, it deals with silty clays and clayey silts, but no evident trend results with reference to the different typologies of products.

DEEP CIRCULATION PATTERNS IN THE NORTH ATLANTIC INFERRED FROM CLAY MINERALOGY AND NEODYMIUM ISOTOPES IN MARINE SEDIMENTS

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Clay mineralogy and neodymium (Nd) isotopic compositions were measured in clay size fractions of Quaternary Labrador Sea sediments in order to constrain the evolution of sedimentary supplies through time in connection with deep oceanic circulation changes. A link between the Western Boundary Undercurrent (WBUC) and the abundance of smectite was observed in modern deep sediments. The smectite/illite ratio (S/I) records changes in the ratio between the smectite-rich supplies

originating from Iceland and Irminger basins and the illite-rich supplies from Labrador Margins. The Nd isotopic signature at sites under WBUC influence displays systematically higher Nd compositions than adjacent sites, in agreement with increasing supplies from the eastern basins through WBUC transport. Therefore, clays and Nd isotopes can be used to constrain changes in

WBUC outflow. Late glacial and deglacial sediments cored on the southern Greenland Rise were analyzed. S/I ratio and Nd signature increased regularly from the late glacial stage until the early Holocene: S/I ratios evolved from 1 to 4 and 143Nd/144Nd ratios from 0.5116 to 0.5120. Both tracers indicate increasing sedimentary supplies from eastern basins since the late glacial stage, reflecting an enhanced westward North Atlantic deepcirculation. Evidence for the inception of the modern deep circulation as early as late glacial stage is also found. Changes in the smectite composition, in agreement with Nd data, may fingerprint sedimentary fluxes driven by distinct water masses: beidellite characterize the North East Atlantic Deep Water, montmorillonite records the Denmark Strait Overflow Water.

MULTISCALE ANALYSIS OF MONTMORILLONITE DISPERSIONS

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Clay suspensions are complex systems with a three-level organization: elementary layers are aggregated in particles; these particles associate in aggregates that aggregate in aggregates' aggregates. To follow the evolution of such systems, it is necessary to conduct a multiscale analysis taking into account all these organization levels. Up to now, each level had to be studied with a different technique: SAXS (Small Angle X-Ray Scattering) gives a quantitative description of the system structure and texture at the particles' level, and TEM a semi-quantitative vision on a larger scale. With the development of a new XRD technique, USAX (Ultra Small Angle X-Ray Scattering, Bonse-Hart setting), we can now have a complete representation of the system between 5Å and 2µm. This is obtained by combination of SAXS (5Å-500Å) and USAXS (300Å-2=µm) spectra. We present here the spectra modelisation method (scale 5Å-2µm) leading to the system's structural and textural parameters at the different organization levels. We will take examples of montmorillonite suspensions in NaCl and KCl solution, and will show that in the case of high-concentration (0.5 N) solutions, the system consists of agregates in wich particles are separated by a porosity of 1500Å to 2000Å, whereas at lower concentration (0.1N), the system consists of isolated layers separated by large distances (about 150Å). This study has been supported by ECOTECH Program grant GS CNRS-ARTEP 95N80/0037.

CLAY MINERALOGY OF JURASSIC/CRETACEOUS SEDIMENTS FROM SVALBARD

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Clay-sized minerals (<2 micrometer) were separated after removal of carbonates with pH 5.0 buffered acetic acid and analyzed by XRD methods. Standard techniques were supplemented with NEWMOD simulated XRD patterns to facilitate the identification of the minerals in this complex assemblage. The samples were collected from the approximately 500m thick Janusfjell Subgroup, a sequence of fine-grained siliciclastic sediments dominated by gray to dark gray shale. In the Jurassic part of this shelf sequence, a fine-grained clay sedimentation took place in partly anoxic conditions that were interrupted periodically by storm generated currents. The Cretaceous section contains evidence of better ventilated depositional conditions and is affected by a southward prograding delta. Quartz, feldspar,and carbonates are the major non-clay minerals present. Secondary jarosite may be common. Despite differences in the field appearance of the sediments, their mineralogical composition is relatively similar. The primary factors influencing the clay minerals present are original sediment composition, diagenesis, and weathering. Kaolinite and illite represent 50 to 75 wt.% of the clay fraction. They are mixed with varying quantities of illite/smectite, illite/chlorite (vermiculite) and smectite/chlorite (vermiculite) including corrensite. Our preliminary results link increased abundance of jarosite with reduced quantities of chlorite-containing materials *indicating that the observed stratigraphic variations are most directly related to the original pyrite content of the sediments and the intensity of modern weathering.Work in progress focuses on probing the possible links between the smectite-rich clays and volcanism related to the opening of the Atlantic Ocean or the impact layer associated with the Mjolnir Crater.*

CLAY MINERALS AND TRACE ELEMENTS IN THE MARINE SEDIMENTS OF THE SICILY SHEL, ITALY

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The clay minerals and trace elements distribution in marine sediments have been investigated as part of studies on the environmental quality of the área off Sicily coast. The research has been focused on the presence of possible contaminated zones and provides data for the identification and future monitoring and control of pollution sources. A granulometric, mineralogical and geochemical study has been carried out on numerous subsurface sediments and some core samples of the shelf.

Taking into account the important role played by fine particles in contamination processes the quality and distribution pattern of clay minerals have been particularly studied. Grain size analyses were made by a combination of wet sieving and sedimentation analysis with a Sedigraph 5000 procedure Quantitative mineralogical determination were made by diffractometric data. Total concentration of Fe, Mn, Zn, Cu, Pb, Co, Ni, Cr were determined on subsamples with grain size less than 0.250 mm. On the whole kaolin, smectite, mixed layer and chlorite appear to be the most widespread clay minerals on the shelf. In the single cores the mineralogical compositions show fundamental homogeneity and some local variations in the kaolin and smectite content can be ascribed to the variations of sedimentary processes.

All the trace element concentrations increase from the coast to the open sea, related to the mineralogical composition of the clay fraction and granulometric size. The resulting values of trace concentrations do not indicate rilevant anthropogenic inputs but permite to distinguish between enrichements related to natural sources and others anomalies not caused by natural factors.

FIBER OPTIC MEASUREMENTS OF TRANSPORT PHENOMENA IN THIN CLAY FILMS

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Diffusive transport of solutes in clays is an important process than may occur in clay barriers. Thin clay films (5-10 thick dry) offer an alternative method for assessing transport on a time scale of minutes to hours. Because of the short time scale the kinetics of adsorption can play a role in the transport phenomena (non-equilibrium transport). Despite the short time scale, the information obtained from transport in thin film often correlates well with data obtained in larger scale experiments where transport is averaged over a wider range of clay structures. Prior experiments were almost exclusively based on an electrochemical detection of the solute using the method of clay-modified electrodes. In this paper we describe the validation of a detection system based on absorption spectrometry which will allow a wider range of solutes to be studied. The system additional allows for a true "sink-source" experimental arrangement. The detection limit was calculated from the signal to noise in the transmitted light (3s) to give a minimum detectable change in absorbance of 0.0084 for Co(bpz)32+ measured at 270 nm. The calibration curve for Co(bpz)32+(A = 0.0056 +5234[M]; r =

0.99997) thus gives a detection limit of 5.2x10-7 molar. For a 50 µL acceptor volume (detector cell) this amounts to 26 picomole. The presence of a high salt concentration results in more rapid transport, apparently the result of between particle transport. Finally, the effect of the addition of organic polymeric materials into the film will be shown.

MINERALOGY AND SIGNIFICANCE OF COLOURED IRON PRECIPITATES IN COASTAL ACID SULFATE SOIL ENVIRONMENTS

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Iron oxyhydroxides, oxyhydroxysulfates and sulfides are important indicators of weathering environments. The relative proportions of these various secondary iron minerals are critically dependant on soil chemistry; in particular, Eh, pH and ionic concentrations. Colour, form, crystallite size and the concentration of substituted cations in iron minerals can be used as quantifiable, environmental indicators. We report on the occurrence, genesis and properties of the wide range of iron minerals formed in soil profiles and associated ochreous precipitates from a variety of undisturbed and adjacent disturbed pyritic mangrove-swamp soils in Australia. In undisturbed mangrove-swamp soils the dominant Fe mineral is pyrite often in the form of framboids and iron oxyhydroxide minerals seldom precipitate. This is indicative of strongly reducing conditions (low Eh). In disturbed mangrove-swamp soils a wide variety of iron oxyhydroxides occur as prominent precipitates of highly-variable colours. This is indicative of wide ranging semi-oxidising (moderate Eh) conditions and ionic concentrations. Dark-reddish-brown precipitates consist dominantly of ferrihydrite and are often embedded or encrusted in sheath-like structures of Fe-oxidising bacteria, mainly Gallionella and Leptothrix. Bright- yellow precipitates are mainly jarosite (pH range 1.5 to 3.5). Yellowish-brown precipitates are mainly goethite. Orange precipitates are mainly schwertmannite (pH in the range 3.5 to 4.5).

CRISTALLINITY INDEXES OF BRAZILIAN SOIL KAOLINITES AS RELATED TO THE INFLUENCE OF PARENT MATERIAL

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The most representative Brazilian soils have kaolinite as the dominant mineral in their clay fraction.Therefore, kaolinite characteristics may strongly influence the chemical and physical properties as well as the management problems of these soils. One of the main characteristics of this mineral is the crystallinity or the degree of order-disorder. The crystallinity of soil kaolinites varies considerably but kaolinites from highly weathered soils are usually disordered. Based on the premise that kaolinite crystallinity could be related to the soil parent material, this study was conducted with the objective of comparing kaolinites from different parent materials in the same climatic region. Two crystallinity indexes or order-disorder criteria were used to compare soil kaolinites from soils derived from granite and from sandstone. The Hinckley crystallinity index (ICH) allowed to distinguish the soils, with the ones from sandstone showing a better crystallization and ICH varying from approximately 0.30 to 0.40. The soil kaolinites from granite showed poorer crystallization with ICH varying from 0.13 to 0.23. The Hughes and Brown index (ICHB) was also used but it did not allow to make a clear differentiation between the two parent materials. ICHB values varied from approx. 4 to 8 in the samples from both parent materials. The width at half height (WHH) for the (001) and (002) peaks showed distinct behavior with the higher values related to the materials from sandstone whereas the materials from granite showed lower values. Consequently, particle size in the [001] direction were inversely related to the crystallinity.

OCCURRENCE OF "TONSTEINS" WITHIN PERMIAN SEAMS FROM RIO GRANDE DO SUL, BRAZIL

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Thin, continuous, extended and kaolinitic levels are interlayered within coal seam of Rio Bonito Formation (Permian) in Parana Basin, Southern Brazil. The coal seams are delimitaed at the top by mudstones and at the base by fine to medium sandstones, interlayered by mudstone levels of 0,80 cm thick. Three"tonsteins"occur: the first one is located within the superior coal seam (1-2 cm) and the others within the inferior coal seam (8-10 cm and 1-3 cm). XRD data show for the "tonsteins"a dominant kaolinitic composition (90%), smectite/illite interlayered (8%) and quartz (2%). The cristallinity index of kaolinite is very high. The REE patterns, chondrite normalized, show an Eu negative anomaly, enrichment of LREE and anomaly, enrichment of LREE and depletion of HREE; the La/Yb ratio, normalized, is 18.31 and Th/U ratio is greater than in the intermediate and superior mudstone. TiO2/Al203 is 0.008; Zn/Al203 is 3.65; Yb/Al203 is 0.013; La/Al1203 is 0.338; Ba/Al203 is 9.14; Ce/Al203 is 0.32; Eu/Al203 is 0.009. All these data suggest a composition related to an acidic volcanism.

SWELLING CLAY MINERALS IN PRIEN LAKE, LOUISIANA, U. S. A.

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Swelling clay minerals represent approximately 50 weight percent of the bottom and sub-bottom sediments accumulating in Prien Lake, a part of the Calcasieu River estuary in southwestern Louisiana. They play a potentially important role in modulating the abundance of organic substances and trace metals in the estuary by ionexchange reactions. The lake waters are oxic with salinities varying from saline to fresh, while the pore waters are sulfidic anoxic. The identity of the minerals in the <2 micrometer fraction was determined by XRD procedures and confirmed by NEWMOD simulation of the patterns. Special treatments used in the identification procedure included K and Mg saturation and expansion with glycerol and ethylene glycol. Mg-saturation restricts the swelling of a 12.5A peak in the air-dried sample to 14A with glycerol, but the peak freely expands to 17A with ethylene glycol. K-saturation restricts the swelling to 14A with both organic compounds. This behavior is interpreted to represent a hydroxy-interlayered vermiculite. This HIV may also be randomly mixed with illite layers in approximately equal proportions.The tendency for this mineral to adsorb hydroxide-forming species is restricted due to the sulfidic nature of the environment. The HIV-clay is not readily identified in the suspended materials entering the lake, but its close affinity to the materials occurring in the soils of the área suggest a detrital origin. The lake bottom sediments also contain detrital quartz (40-50 wt.%) and feldspars (<10 wt.%) and approximately 5 wt.% authigenic pyrite. Gypsum and calcite are rare components of thesediment.

BACTERIA AND MIXED Fe-Si AND Fe-Mn MINERALS: TEM/EDS STUDY OF SAMPLES COLLECTED NEAR HYDROTHERMAL VENTS (SOUTHERN EXPLORER RIDGE) IN THE NORTHEAST PACIFIC OCEAN

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Samples of dark or orange coatings on aphyric basalt outcrops were collected near the Magic Mountain hydrothermal deposit in the Southern Explorer Ridge.

Transmission electron microscopic observations of thin sections revealed fine mineral particles of various morphologies (i.e., crumpled sheets, nodules, filaments,amorphous concretions and detrital silica fragments), along with diatom fragments and remnants of bacterial cells. Cell wall structures were not well preserved, and often appeared to be replaced by minerals. Energy dispersive spectroscopic analyses indicated that most minerals found in association with bacterial remains were iron- and silicon-rich. In many samples, the Fe/Si atomic ratio of the crumpled sheets, filaments, nodules and amorp hous concretions was close to 1, but somesamples contained similar amounts of

Fe and Mn with very little Si. These Fe-Mn-rich precipitates were mainly found in samples described as black coatings. The microcrystalline nature of the precipitates prevented positive identification by electron diffraction. Bacteria are known to be present near hydrothermal vents where they obtain energy from a wide range of organic and inorganic substrates; however, their role in the formation of the authigenic minerals remains uncertain. One may speculate that they served as a substrate for metal binding and mineral nucleation in an aqueous environment rich in dissolved species. Recent studies also suggest that bacteria play a role in rock weathering, and might contribute to the dissolution of the underlying basalt, forming new Fe-Si and Fe-Mn minerals.

HEMATITES OF VARIOUS CRYSTALLINITY AND SMECTITES IN THE HOT BRINE SEDIMENTS OF THE RED SEA

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Much is known about the smectites formed in the Fe-rich hot brines of the deeps in the Red Sea but very little about the FeIII oxides. A 4m thinly bedded core was mineralogically analysed by XRD, Mössbauer spectroscopy (MS) and other methods. Besides goethite and akaganeite, hematite and Fe-rich smectites dominated the 16 samples. Nanohematite was identified in the upper and coarse hematite in the lower core, each of which was tentatively further bipartitioned by MS (table,MT=Morin transition). TEM of nanohematite shows particles ca. 5 nm in size and XRD exhibits strongly expressed anisotropic line broadening indicating reduced crystal growth parallel to c. In contrast, the coarse hematite consists of idiomorphic, hexagonal plates 60 to 200 nm across. Some small amounts of a cubic phase may be responsible for some magnetic susceptibility at RT. EM microanalysis distinguishes particles with essentially Fe from those with some Si. Nano-hematite also differs in its IR spectrum from coarse hematite. The associated smectites are low in Al and either high in Fe and low in Mg of vice versa. The Fe rich variety partly orders magnetically at 4.2 K, is trioctahedral and soluble in oxalate. Synthesis experiments are under way to explain the genesis of the large range of hematite crystallinity in the brine.

CLAY PILLARING PROCESSES IN PROGRESSIVE CONCENTRATED CONDITIONS

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Usually, pillaring is carried out on dilute medium i) the clay was in aqueous diluted suspension and ii) the pillaring solution is also in low Al13n+concentration. Handling such large volumes of liquid is not suitable for industrial approach. The aim of this study is to use as little liquid as possible in obtaining clay pillaring. Two bentonites from Wyoming and Tunisia are used to compare their pillaring with progressively more concentrated conditions both for the clay suspension and for the pillaring solutions. We start from a diluted pillaring solution ([Al3+] = 0.1M) which is added to an aqueous 2%w/w clay suspension. This classical method leads to a dispersion of clay in the total suspension of 0.4%. An opposite method is used where the dry powder clay is added to the pillared diluted solution. This does not affect the final concentration (0.5%) but this improves the grinding of the obtained pillared clays. In order to obtain a more final concentrated clay dispersion, we try to put the powder clay into a concentrated pillaring solution (2M). This leads to a final concentration up to 25%. Thinking about the recuperation of the solid and in order to avoid further liquid separations, the clay is introduced in dialysis bags as paste(50% w/w) or as dry powder and plunged into diluted or concentrated pillaring solutions. Pillaring always occurs with the different methods and with the different clays (d001 at about 18Å). All the samples show a thermal and remarkable ageing stability.

THE DEHYDROXYLATION OF INTERCALATED KAOLINITES: AN INFRARED EMISSION SPECTROSCOPIC STUDY

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The dehydroxylation of an ordered kaolinite and its intercalates, has been investigated by Fourier transform in-situ infrared emission spectroscopy over a temperature range of 100 to 600 oC at 25 degree intervals. The major advantage of the IES technique lies in the ability to obtain vibrational spectroscopic information in-situ at the elevated temperature. Dehydroxylation at the selected temperatures was studied by the loss of intensity of hydroxyl stretching bands. The infra red emission spectra show intensity at 3677 (2), 3648 (3), and 3623 (5) cm-1. It is proposed that the emission process favours the 2 and 3 bands, as these bands are the out of phase hydroxyl stretching modes. Bands at 3684 and 3695 cm-1 were not observed in the IES spectra of ordered kaolinites. The kaolinite clay mineral loses the inner sheet and inner hydroxyl groups simultaneously, except at the final dehydroxylation stage where the outer hydroxyl group is lost and some of the inner hydroxyl group remains. This is evidenced by the intensity loss of the ~3665 cm-1 peak, before the inner hydroxyl groups as determined by the intensity loss of the~3620 cm-1 peak. The 2 and 3bands show a blue shift whilst 5 band shows a red shift. The bands show a decrease in band widths as the kaolinite is dehydroxylated.

The potassium acetate intercalate dehydroxylates at lower temperatures than the urea intercalate or the untreated kaolinite. The changes in dehydroxylation temperatures are interpreted in terms of the mechanism of kaolinite dehydroxylation.

ORGANIC ACID- MONTMORILLONITE ADSORPTION USING DIFFUSE REFLECTANCE INFRARED SPECTROSCOPY

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Organic acids bind to montmorillonite in two ways, either by dipole interaction with oxygens in the interlayer space, or by bonding of carboxylate anions to exposed aluminium ions. Diffuse Reflectance Fourier Transform Infrared (DRIFT) spectroscopy was used to monitor the sorption of propanoic acid by montmorillonite.Infrared spectra of saturated aliphatic carboxylic acids show strong bands around 1730 to 1700 cm-1, corresponding to the C=O stretching vibration (C=O)s. Salts of these acids have bands ~1620 to 1550 cm-1 and 1400 to 1300 cm-1 corresponding to the asymmetric and symmetric O-C-O stretching bands ((O-C-O)a and(O-C-O)a), of the carboxylate anion. The DRIFT spectra of the propanoic acid - montmorillonite complexes have bands at 1718 and 1548 cm-1, assigned to (C=O)s and (O-C-O)a and attributed to physical, and chemical adsorption of the acid, respectively. For increasing acid concentration, the peak área of (C=O)s showed a linear increase and the peak área of (O-C-O)a showed a linear increase levelling to a maximum, corresponding to saturation of available binding sites. For a calcium montmorillonitic clay the adsorbed carboxylate anion concentration reached a maximum of 0.54 mol.kg-1. Comparison of the separation of the asymmetric and symmetric (O-C-O) bands for the propionate-montmorillonite complex and sodium propionate indicated a bridging complex was formed in the acid-clay complex. This value enabled the number of binding sites on the clay crystal to be calculated as 6.6 x 1023 per kg.

STRUCTURAL ASPECTS OF HISINGERITE - A VIBRATIONAL SPECTROSCOPIC STUDY

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Hisingerite is a rare mineral, recently interpreted to be the iron analogue of spherical halloysite. On heating, it shows three maxima of H2O loss: about 6% at 150¡ and smaller amounts at approximately 270¡ and 320¡ totalling a further 6%. Raman, FTIR reflectance and Infrared emission techniques have been used to assist in the elucidation of the structure of this poorly crystalline hydrous iron silicate. Drift spectroscopy shows strong OH vibrations at 3550 cm-1 with bands in the low *frequency region at 1625, 1020, 670, 480 and 450 cm-1. Raman spectroscopy shows a broad band centred at 950 cm-1 and additional bands at 690, 540, 420 cm-1. The IR bands at 3550 and 1625 cm-1 are attributed to water in the Hisingerite structure. The absence of Raman bands at these positions supports this assignment. The band at 670 in the IR and at 690 cm-1 in the Raman is assigned to the FeOH librational mode. The band at ~1000 cm-1 is attributed to the SiO stretching vibrations. Infrared emssion spectroscopy has been used to confirm these assignments. IES shows the loss of the water vibrations at ~150 °C, corresponding to the DTA 150 °C endotherm and the loss of the hydroxyl group over the temperature range 200 to 400 °C, corresponding to the broad endotherm between 270 and 320 °C. The 690 cm-1band is retained up to 400 °C. The bands at 480 and 450 cm-1 are attributed to Fe-O-Si vibrational modes.*

HYDROGEN BONDING IN KAOLINITE-A RAMAN AND XRD STUDY

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The structure of kaolinites, obtained from a wide variety of sources, has been studied using both Raman microscopy and X-ray diffraction techniques. The Raman spectra of the hydroxyl stretching region were both sample and orientation dependent. Kaolinites can be classified into two groups according to the ratio of the Raman intensities of the 3685 and 3695 cm-1 bands of the inner surface hydroxyl groups. Two predominant kaolinite groups were obtained based on this ratio. In comparison with X-ray powder diffraction, no relationship was found between the d-spacing and the crystal domain size (CDS, which was measured using the Scherrer equation), measurement from the (001) reflection (c-direction) and the Raman spectral intensities thereby indicating the Raman spectra are independent of the thickness of the layers and the number of stacked layers. However, a relationship of the CDS in the a-b direction and intensities of the 3685 and 3695 cm-1 bands was found showing that the relative position of one layer to the other determines the position of the inner surface hydroxyl groups and the hydrogen bonding with the oxygen of the opposite layer. A hypothesis based on symmetric and non-symmetric hydrogen bonding of the inner surface hydroxyl groups is proposed to explain the two inner surface hydroxyl bands centred at 3685 and 3695 cm-1. The bands at 3670 and 3650 cm-1 are described in terms of the out of phase vibrations of the in phase vibrations at 3695 and 3685 cm-1.

SYNTHESIS AND CHARACTERIZATION OF HECTORITE-QUATERNARY AMINE HYBRID

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The starting material for synthesis of hectorite-quaternary amine hybrid consisted of silica sol, aminosilane, LiF and Mg(OH)2 gel. (We use the term " hybrid" for the complex of inorganic and organic materials which are connected by chemical bonds each other.) The mixture was sealed in Au capsule and treated at hydrothermal conditions of 200 oC and 100MPa for 1-5days. X-ray diffraction pattern of the hydrothermal product showed that hectorite was formed with small amounts of amorphous phase. The basal spacing of the hectorite did not change with the change in humidity, and the sample was well dispersed in toluene. These suggest the hydrophobic and organophillic nature of the hectorite interlayer. In infrared spectra of the product, the Si-C and C-C bonds, like the aminosilane, were confirmed

suggesting that there was no pyrolysis during the hydrothermal treatment. The absorption peak attributed to other organic bonds was not observed. Furthermore, by nuclear magnetic resonance, Si-O-Si-C bond was confirmed to exist in the sample. Integrating all observations, it can be concluded that the quaternary amine fragment is in the interlayer of the hectorite fragment and is combined directly with silicate sheet, that is, "Hectorite-Quaternary amine hybrid" was synthesized.

KAOLINITE BEHAVIOUR TO INCREASING PRESSURE. GENETIC CONSIDERATIONS

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Kaolinite of medium-high crystallinity was isostatically and uniaxially pressurized up to 20.0 kbar for 10 min. The increased pressure caused kaolinite to lose crystallinity as measured by XRD and IR. The structural disorder was mainly associated to interlayer shifts of the b/3 type. In the experiment, isostatic pressure proved more effective than uniaxial pressure in increasing disorder; thus, the degree of disorder resulting from a 2 kbar isostatic pressure was equivalent to that caused by a 3.2 kbar uniaxial pressure. Also, the effect of a high pressure was similar to that obtained with lower pressures applied several times (e.g. the effect of applying a 8.5 kbar pressure for 10 min was comparable to that of using a 3.2 kbar pressure 5 times). Above 1.0 kbar, kaolinite crystals gradually lost their hexagonal morphology, edges were rounded, layers were fractured and distorted, and sheets in book-like stacks glided and rotated, all these leading to decreasing particle size and increasing surface área. Because the pressures used in this experiment can occur in burial diagenesis and low-grade regional metamorphic processes, and rocks from these facies usually exhibit well-ordered kaolinite of a large particle size, one can assume temperature (and the presence of fluids) to induce crystal growth from disordered microcrystals with a high surface activity.

ACIDIC PROPERTIES OF A POROUS CLAY HETEROSTRUCTURE

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A new family of porous clay heterostructure (PCHs) was prepared by templated gallery synthesis of mesoporous silica in smectite clay. Using cetyltrimethyl ammonium cation (CTMA) as the exchange cation in fluorohectorite (FH), neutral decylamine as the co-surfactant and TEOS (tetraethylorthosilicate) as the silica precursor we obtained a FH-PCH with a surface área in the range 555-790 m2/g with a pore size between 19 and 23 depending on the calcination temperature. The hydrolysis of the inorganic neutral silica precursor in the gallery influences the ordering of these co-surfactants into micellar organic/inorganic rod arrays, similar to the emplating mechanism for mesoporous MCM-41 molecular sieves. Calcination not only removes the organics but also induces great acidity in the material in the range 300-450C. The ehydration of 2-methyl-3-butyn-2-ol (MBOH), pyridine adsorption and pH measurements were used to characterize the acidic properties of these materials and results were compared with lumina-pillared fluorohectorite, K-10 montmorillonite and pure silica MCM-41. The acidity arises in part from lattice hydrolysis of FH and by generation of protons from the degradation of the quaternary ammonium cation and needed to balance the charge of the layered host.
Calcination of FH-PCH upon 450C results in the further crosslinking of the gallery silica mesostructure and the clay layers andt his gives rise to reduced acidity and diminished MBOH conversions.

ORIENTATION OF 6-BENZENE IN THE INTERLAYER OF MODIFIED CLAYS

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Polarized IR dichroism results indicate that the orientation of trimethylphenylammonium (TMPA) in the interlayers of smectites is such that the phenyl-N bond is parallel to the 001 surface. For smectites with tetrahedral charge, the phenyl ring-plane is normal to the 001 surface and loses orientational preference as tetrahedral charge decreases and octahedral charge increases. The orientation dependence of TMPA with density and location of layer charge indicates that mineral structural factors are important in controlling solution-phase reactions at mineral surfaces. To better understand these factors, we studied the vapor phase sorption of 6-benzene onto oriented films of several smectites, encompassing a wide range of charge and charge location properties, loaded with TMPA at 0, 25, 50, 75%, and 100% of the cation exchange capacity (CEC). For all smectites and at all TMPA loadings, two sorbed forms of 6-benzene were noted and TMPA loading influenced which form dominated. At 100% CEC loadings, benzene sorption depended on the overall charge of the smectite. At low TMPA loadings (0-25% CEC), interlayer water associated with Na+ out-competed benzene, while at intermediate loadings (50-75% CEC) benzene preferentially sorbed. An absorption band for C-C in-ring stretch at 1330 cm-1indicated that a pure benzene phase existed. However, this band was strongly dichroic at TMPA loadings of 25 and 50%.
Our results indicate that individual benzene molecules within the neat phase stacked preferentially with one another such that the benzene ring-plane was nearly normal to the 001 face of the clay.

MECHANISMS FOR INTERACTIONS OF ORGANIC MOLECULES AND CLAY PARTICLES IN AQUEOUS SUSPENSION

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We have studied the interactions between cationic dyes and clay particles in aqueous suspensions, using spectrophotometric techniques.. We have used natural and synthetic montmorillonites and hectoriteswith azinic, thiazinic and similar cationic dyes. These dyes have a great affinity for the clay surface, very high molar extinction coefficients, and characteristic methachromatic and acid-base behaviour. These properties make them suitable to be used as spectrophotometric probes to study systems containing clay particles in suspension. The changes detected in the time evolution spectra of the adsorbed dyes employing different time scales, from minutes to month, can be associated to different processes involving dye-particles and particle-particle interactions. Adding the dye molecules to the suspension, they former readily adsorb on the external surfaces of the clay particles. The local concentrations increase significantly and dye aggregates are readily detected. As time passes, the dye molecules migrate to the interlamelar spaces, and protonation occurs due to the high acidity of this region. As this migration proceeds, the aggregates are transformed into smaller aggregates and monomers. These processes occur typically within the minute to hours time scale. At longer times (days and weeks), processes involving particle-particle interactions take place, creating new environments at which the dye molecules are located, as evidenced by the absorption spectra of the suspension. Although the rate and magnitude of these processes depend on conditions like concentration, presence of electrolytes, etc., emphasis will be given to factors related to the clay and dye natures. Examples will be given for representative dye-clay systems for which different processes predominate.

THE INFLUENCE OF ELECTROLYTES ON THE INTERATIONS BETWEEN CATIONIC DYES AND CLAY PARTICLES IN SUSPENSION

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The interaction of several cationic dyes with different clays (natural and synthetic montmorillonites and hectorites) have been systematically studied. The variation with *time of the electronic absorption spectra of the dyes adsorbed on the clay particles lead to the detection of several processes involved in the dye-clay interactions.*

The clay particles and the dye molecules are charged, and the ionic strength of the medium certainly plays an important role in the dye-clay interactions. In order to investigate the influence of electrolytes on these interactions, two representative dye-clay systems, methylene blue-montmorillonite SWy-1 and MB-laponite RD were selected and studied in detail, in the absence and in the presence of electrolytes. In the absence of electrolytes the spectral time evolution of these two dye-clay systems are quite different, reflecting the different processes controlling the dye-clay and particle-particle interactions. In the presence of electrolytes the spectral time evolution becomes essentially the same, indicating that under these conditions the same processes are occurring in both systems. Processes involving particle-particle interactions predominate when electrolytes are added to the suspension, while in the absence of electrolytes changes due to the migration of dye molecules from the external to the internal surfaces predominate. Models to explain the changes observed in these systems will be presented. It should be noted that in many studies on similar systems reported in the literature, buffers are extensively used. Our results indicate that caution should be taken to interpret correctly the experimental results in this case.

ORGANOPHILIC CLAYS: MODELS

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The ability of organoclays to form stable dispersions or gels in organic solvents, depends upon the surfactant amount adsorbed on the clay surface. Following step by step the isotherm of quaternarisation of a montmorillonite, in aqueous medium, we try to give a model of the microstructure of the modified clay. We used several complementary methods (SAXS, XRD and TEM) to show how the surfactant behaves towards the phyllosilicate surface. Adsorption isotherms show that an amount of surfactant adsorbed up to the equivalent to the CEC (cationic exchange capacity), the adsorption process is a classical exchange of the compensator cations of the clay by quaternary ammonium cations. At this point, XRD diffractograms on powder and paste, give a d001 equal to 18 Å. The possible conformation of the surfactant is a bilayer, in which the mnolecules lie flat on the clay suface. Beyond this amount, the increasing adsorption matches with more lateral alkyl chain interaction, up to a quantity equivalent to about 2 CEC. The corresponding XRD diffractograms are the superposition of two structure: of the clay mineral (22 Å) and of the crystallized surfactant (20 Å). In that case, the surfactant located in the interlamellar space is more tilted that in the previous case. Moreover, the appearance of thin peaks of surfactants means that they are desorbed. The ammonium cations organize in an independant structure, which looks like a lamellar phase. In fact, two lamellar species are in coexistance. Static models are presented to support the understanding of the redispersion mechanism of organophilic clays in organic media.

PHYSICOCHEMICAL AND CATALYTIC PROPERTIES OF PROTEINS AND ENZYMES ADSORBED ON SMECTITES AND VARIABLE-CHARGE MINERALS

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Adsorption of proteins and extracellular enzymes occurs when they come in contact with soil colloids. After adsorption, protein availability as nutrient source for microbial growth and the catalytic behavior of enzymes may be totally or partially changed. Smectites, metal oxides, and variable charge minerals, i.e. clay coated by

OH-Al or OH-Fe, are very abundant and may be substantially involved in protein adsorption. Protein adsorption is influenced by such factors as surface properties, nature and properties of the protein, and solution conditions. This work stuied the adsorption of proteins (catalase, albumin, pepsin, and lysozime) and enzymes (invertase, urease, and phosphatase), with different molecular weights, isolectric points and catalytic activities on three smectites (two montmorillonites and one hectorite), on montmorillonite and hectorite coated by hydroxy Al species (OH-Al), and on aluminum and iron oxides. Usually, Na-saturated montmorillonite adsorbed higher amounts of proteins than Ca- or Mg-saturated clay. Furthermore, the adsorption was most pronounced near the isoelectric point of each protein.

When clay surfaces were coated by OH-Al- or OH-Fe-species a decrease in protein adsorption and reduced activity of adsorbed enzymes were measured. As inferred by X-ray diffraction, interlayering of proteins in smectites was prevented by the OH-Al species. pH and the nature of buffered solution strongly influenced adsorption of invertase and urease on Na-montmorillonite, aluminum oxide and Al(OH)x-montmorillonite complexes. By increasing pH from 4 to 9, the amount of both enzymes adsorbed decreased considerably. Furthermore, pH-adsorption profiles differed when acetate or phosphate solutions were used as buffers. Much more enzyme was usually adsorbed in the acetate than in phosphate systems on all the minerals used.

CLAY MINERAL- AND ORGANIC DIAGENESIS OF THE LOWER OLIGOCENE FISCHSCHIEFER, MOLASSE BASIN, AUSTRIA

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The so-called Fischschiefer formation (Latdorfian, Lower Oligocene) has been identified as the likely source rock for petroleum in the Molasse Basin of Austria. The Fischschiefer-shales are in fact clay marls, varying in thickness up to 30 m. The depth of the Fischschiefer horizon increases from north to south, because it was partly overthrusted by the nappe system of the limestone Alps. Ten samples from geographically different positions of the Molasse Basin and covering a depth range from 1242 m in the north to 4294 m in the south were investigated for their mineralogical and chemical compositions. In addition the coexisting organic matter was investigated to characterize changes in organic maturity parameters with depth during diagenesis. The mineralogical composition of the bulk samples showed that the sediments are derived from the north, the Bohemian Massif. They are low in quartz, high in kaolinite and calcite, except for three samples, which are silicified. In the < 0.2 µm fraction the illitization of the mixed layer illite/smectite can be observed. The illite content in I/S ranges from 45% for the shallowest sample to 82% for the deepest sample. The I/S mixed layer minerals show no ordering, which may have been inhibited by the presence of substantial organic matter during the illitization process. The illitization trend was correlated with various organic maturity parameters, including total organic C, vitrinite reflectance and Rock-Eval pyrolysis parameters.

INFLUENCE OF THE GROWTH PHASE OF BACTERIA ON THEIR ADHESION TO MINERAL PARTICLES

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The most hydrophilic bacteria (as measured by contact angle determination with drops of water) can be transported the most readily through beds of sand. We find that bacterial surface hydrophilicity varies significantly with the growth phase: bacteria grown in the log and decay phases are more hydrophilic than bacteria harvested in the stationary phase. By contact angle measurements with several different apolar and polar liquids and by electrokinetic measurements the complete surface-thermodynamic properties of the common bacterium Pseudomonas aeruginosa can be determined for all three growth phases. The surface-thermodynamic properties of a vast array of clay and other mineral particles and surfaces are now known. From these data, the free energies of interaction of the bacterium with various mineral particles, immersed in water, can be calculated. The magnitude and sign of these free energies allow the prediction, e;g., that for the different growth phases of Ps. aeruginosa, interacting with dolomite particles, the bacteria harvested from the log or the decay phase would repel these particles, whereas Ps. aeruginosa, obtained from the stationary phase, should adhere to them. Subsequent transport experiments with these different microbial suspensions through columns of dolomite particles showed that more than 50% of the organisms harvested from the stationary phase were retained by the dolomite particles, whilst only about 10% of the organisms from the two more hydrophilic bacterial phases passed unhindered through the column.

FORMATION OF SMECTITES AND THEIR ALTERATION IN TWO CHRONOSEQUENCES OF PODZOLS IN FINLAND

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Pedogenic formation of clay minerals were studied in two sequences of podzols of increasing ages. The first sequence was selected in Central Finland and made with podzols developed from till materials, the other sequence is made of podzols developed from fluvioglacial sands in North Finland. Age of soils was estimated according to altitude above the present sea level with reference to age of ancient shorelines and rate of land uplift. Ages of podzols increase from 5 500 to 10 000 years for the sequence from tills and from 320 to 9 300 years for the sequence from fluvioglacial sands. Clay minerals in fine (< 0.1 µm) and coarse (0.1-2 µm) fractions were studied by X-ray diffraction. Layer-charge of expandable minerals was estimated on the basis of CEC measurements and re-expansion with ethylene glycol following K-saturation and heating to 110°C. The same pedogenic transformations of clay minerals were observed for the podzols of the two sequences.
Dioctahedral smectites with large tetrahedral substitution were formed in podzols older than 6 500 years when developed from tills, whereas only 3 200 years were required to produce smectites from fluvioglacial sands. So, formation of smectite in eluvial horizon of podzols is faster in sandy materials than in podzolized tills. This could be attributed to a faster drainage in fluvioglacial sands. For all the podzols the layer-charge of the smectites decreases with time; low-charge smectites were observed in the podzols older than 9 000 years, suggesting alteration of smectite with time.

CLAY MINERALS OF POST-MAGMATIC PROCESSES IN TWO TYPES OF BASALTIC FLOWS IN THE PARANA BASIN

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Twelve basaltic flows make up a 20,000 km rock pile in the north part of Rio Grande do Sul - Brazil, representing the tholeiitic flood volcanism of Cretaceous Parana basin. 15 to 35 meters thick flows (type I), characterized by an inner macrovesicular level with amethyst mineralization, intercalate with 30 to 50 metres thick, highly fractured and non mineralized flows (typeII) in the volcanic pile. The type I flows have plagioclase, augite, Ti-magnetite and olivine and differ from type II, which have two pyroxenes, augite and pigeonite, and no olivine as main mineral components. Post-magmatic processes and hydrothermal alteration are responsible for the formation of clay minerals which occur in the groundmass, in the interstices of the matrix grains, filling vesicles and fractures and also in the alteration of olivine and pyroxene. The kinetic, temperature and chemical conditions are responsible for the compositional differences of the clay minerals. In the fast cooling parts of the rock, like fractures and vesicle borders, saponite is the stable clay mineral. In the inner zones, where the cooling is slower, interstratified smectite-chlorite occur, specially originated from the cristalization of the interstitial residue in the rock matrix and also in the internal parts of the vesicles. The alteration of olivine forms celadonite in type I flows. In the type II flows, the pyroxenes are less altered, forming saponite. Celadonite and quartz are the mineralogic post-magmatic association of the type I flows; K-feldspar, quartz and saponite are common in type II flows.

CORRELATION BETWEEN THE MOST FREQUENTLY USED XRD CRYSTALLINITY INDICES FOR KAOLINITE. THEIR ACCURACY AND REPRODUCIBILITY

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The degree of structural order in kaolinite is highly relevant to its industrial applications and genesis. This has fostered the search for a straightforward, expeditious procedure for quantifying order in kaolinites, which has materialized in various relations known as "kaolinite crystallinity indices" (KCI) derived from XRD data. The purpose of this work was to assess the accuracy and reproducibility of KCI values as determined by X-ray diffraction (XRD), using kaolinites of different degree of structural order. The crystallinity indices of Hinckley, Range & Weiss, Liètard, Stoch, Hughes & Brown and Amigó et al., and the expert system of Plançon & Zacharie, were evaluated in this respect. One of the most important conclusion of this study is that there is a high correlation between the following indices: Hinckley and Stoch (-0.98), Hinckley and Range & Weiss (-0.84), Hinckley and Amigó (001) (-0.74), Stoch and Range & Weiss (0.92), Liètard and Amigó (002) (-0.72), and Amigó (001) and (002) (0.83). As a result, each of these indices can be used to predict the other in the previous couples. On the other hand, the expert system is only correlated with the Hinckley (0.85) and Amigó (001) indices (-0.80). Also, for reproducible KCI values to be obtained, XRD measurements should be replicated at least five times.

Rb-Sr SYSTEMATICS OF NEOPROTEROZOIC SHALES, VARANGER PENINSULA, NORTH NORWAY

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Eighteen clay subfractions (SFs) in narrow size-ranges from 1-2 mu down to 0.1-0.2 and <0.1 mu have been separated from shales of the Stangenes (U.Riphean), Nyborg and Stappogiedde (Vendian) Formations. The coarser SFs include some 2M1 illite as well as the usual 1M polymorph. The finer SFs contain only the 1Md illite. After leaching with NH4OAc, Rb-Sr "leachochrons" for untreated SF, leachate and residue were derived for all SFs. As the clay particle size decreases from 1-2 to 0.1-0.2 mu: (1) The proportion of chlorite, where present, is reduced; (2) The CIS increases; (3) The 87Rb/86Sr ratio in the residues increases; (4) The *apparent Rb-Sr age and 87Sr/86Sr initial ratio vary smoothly. In addition, the data points of residues are aligned linearly on both the 87Rb/86Sr - 87Sr/86Sr and the 1/Sr - 87Sr/86Sr diagrams. These results show that a mixture of at least two, non-cogenetic, illite generations is present in each shale; and the illites crystallized in environments with dissimilar 87Sr/86Sr ratios. The end-members of the mixture are the 2M1+1M detrital and 1Md authigenic illite for the Stangenes shale, and the authigenic 1M and 1Md illites for the Nyborg and Stappogiedde shales. The minimum Rb-Sr ages of early burial diagenesis are c.650, 550 and 530 Ma for the Stangenes, Nyborg and Stappogiedde Formations, respectively. The 440-390 Ma ages of the 0.1-0.2- and <0.1-mu SFs in the Nyborg and Stappogiedde Formations appear to relate to Scandian uplift or deformation phases. This work was supported by the Geological Survey of Norway and the RFBR Grant 96-05-65915.*

NUCLEAR MAGNETIC RESONANCE STUDY ON AQUEOUS SUSPENSIONS OF NATURAL AND SYNTHETIC CLAYS

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This contribution deals with the orientation of water molecules near the clay surface, the formation of tactoids in clay suspensions and with alkali-tetraalkylammonium cation competition to interact with the solid surface. Variation of the residual quadrupolar splitting of water deuterons results from the change of water orientation relative to the director coordinate system associated to the clay interface. This method has been applied to suspensions of natural clays (montmorillonite, hectorite, saponite and beidellite) and synthetic saponites with different layer charges per unit formula. Two mean orientations of interfacial water molecules, associated to the clay surface or counterions, are deduced from these splitting data. The applicability and the limits of this approach are described. Water deuteron splittings are also related to the amount of interfacial molecules. Thus, the formation of clay aggregates influences the deuterium line separation. The dependence of the layer charge and the nature of counterions on the relative size of tactoids are reported for suspensions of synthetic saponites. Competition experiments between alkali and tetrapropylammonium cations indicate that the removal of inorganic cations from the neighbourhood of the clay surface and alkali NMR visibility depend on the layer charge of saponites.

INTERACTION OF NONIONIC SURFACTANTS AT A CLAY INTERFACE

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We have studied phenomena occurring at the interface of synthetic saponites suspended in aqueous solutions of polyethyleneglycol monoalkylethers. The behaviour of solvent, surfactant molecules and counterions has been investigated by nuclear magnetic resonance (NMR) spectroscopy. This method is quite informative since several probe nuclei such as 2H, 17O, 7Li, 23Na, 1H or 13C can be observed, and different parameters can be determined. Residual quadrupole splittings define the mean orientation of species near the clay surface whereas relaxation parameters are related to the surroundings and mobility of the observed nuclei. Surfactant molecules affect the mean orientation of interfacial water molecules as well as the environment and dynamics of counterions. A less symmetric surroundings of cations together with a decrease of its motion can be inferred from these NMR data. Accordingly, mobility of surfactant molecules is reduced by the presence of clay. This work also shows how the clay charge and the nature of counterions influence the properties of interfacial species. These data have been extended to surfactants with different monomer units and/or with different alkyl chains. These observations have been later complemented by other techniques such as Raman or Infrared spectroscopy.

OCCURRENCE OF ILLITE IN CLAY PODS IN #29 MINE, VIBURNUM TREND, SE MISSOURI

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Clay-rich bodies termed "clay pods" are localized in the north portion of #29 Mine which is the northern-most Viburnum Trend MVT Pb-Zn mine. The pods are associated with bleached host-rock dolomite and consist primarily of detrital illite and K-feldspar (adularia) dissolved from lower Paleozoic carbonate rock and/or disaggregated from overlying shale. Pod material in some locations is stratified, indicating transportation and deposition by fluids. The authigenic minerals in the clay pods include dolomite, sulfides (pyrite and/or marcasite), illite, and less commonly quartz + K-feldspar. Fluid inclusions in authigenic quartz from bleached dolomite have a modal homogenization temperature of 167°C. The modal weight percent equivalent of NaCl is 17%, suggesting a basinal brine. The 1.0 - 0.5 μm e.s.d. of clay pods is >90% 1Md illite and <10% K-feldspar and/or 2M1 illite. The < 0.5 μm e.s.d. is nearly pure 1Md. Illite in both size fractions is R3 ordered with < 5% smectite layers. 2M1 illite, if present, is detrital and the 1Md illite is thought to be a mixture of detrital and authigenic based on SEM observations and K/Ar dating.
The authigenic clay pod illite may well have formed from the same hydrothermal fluids as the authigenic quartz.

THE EFFECT OF MINERALOGY ON THE DISPERSION OF SODIC SOILS BEARING EXCHANGEABLE GROUP II CATIONS

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The effect of magnesium on the dispersion of clay from soil has long been a source of contention. Most studies have concentrated on the effects of magnesium on hydraulic conductivity and infiltration rate but relatively little attention has been given to the fine mineralogical distinctions between soils. A major aim of this current study was to observe differences in the dispersive behaviour of six Australian soils, with different clay mineralogies, which resulted from exchangeable sodium in combination with different exchangeable group II cations. Soils with ESP values in the range 0-20, but otherwise saturated with Mg, Ca, Sr or Ba, were assessed for dispersive behaviour using mechanical treatments with a range of energies. Results indicate that soils with more than 20% randomly interstratified material (RIM) displayed enhanced dispersion when exchangeable Mg was present; in particular, one soil dominated by RIM showed greater responses to Mg than any of the others. Kaolin-smectites were important components of the RIM present in these soils. With a decrease in the percentage of RIM, the effect of Mg on soil dispersion decreased. Soils dominated by illite displayed only small responses to Mg, and generally showed poor stability towards mechanical disruption, regardless of exchangeable cation. A highly smectitic soil was particularly stable to the effects of dispersion. It seems possible that the response of a soil to the presence of Mg could be predicted from its mineralogy and ESP.

CLAY MINERALS AS AN INDICATOR OF ANCIENT WEATHERING PHENOMENA OF THE PRECAMBRIAN ROCKS, ALDAN SHIELD, RUSSIAN FEDERATION

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Clay minerals from weathering profiles, observed on and within Precambrian rocks of the apatite deposits, have been investigated from the view-points of geology, mineralogy, pedology. Weathering phenomena of rocks have been recognized in the Fedorovskaya and Gorbylikhskaya Formations of the Aldan Shield. Two complexes that differ in rock composition and structure are involved in the geological sections of the deposits. The lower complex (basement) is a stratum (up to 500m) of interlayered gneisses, schists and apatite-bearing carbonate and calc-silicate rocks. The upper complex (up to 200m) is a blanket-like residual deposit of intensely crushed and strongly altered formations of the basement. Clay minerals (hydromica, vermiculite, chlorite, illite, kaolinite) are predominantly developed in the upper complex of the deposits, whereas in the lower complex they occur dissipated as separate crystals or concentrated in layers and nests mainly in the apatite-carbonate rocks. The carbonate rocks are typically medium-grained, massive, mottled or banded, and red-brown in color. Their oxidized character is expressed by high Fe3+/Fe2+ ratio. The banded structure is due to throughgoing bands a few millimeters to several decimetres in thickness. Some of the mottled rocks contain pocket-like isolation and thin beds rich in clay, hematite, and apatite and seem to be of karstic origin. The isotopic data for the carbonates from coexisting poor and rich in clay minerals bands are similar to those under- and overlying massive carbonates. It is consistent with the proposed models of simultaneous chemogenic and detrital deposition and intraformational erosion during weathering process.

ZEOLITES AND HUMAN HEALTH: COMPARISON OF MECHANISMS FOR ASBESTOS- AND ZEOLITE-INDUCED DISEASES

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Like asbestos (particularly the amphibole varieties of asbestos), erionite has been linked to high incidences of disease in the respiratory tract and pleura of humans and animals. Much of the initial focus on mechanisms of erionite-induced diseases centered on the fibrous morphology of erionite as an important factor. However, differences in the biological activities of various fibrous silicates--including the asbestos minerals (which show a wide range in activity), erionite (which appears to be more active than asbestos), and other fibrous clays and zeolites (which are generally less active than asbestos)--suggest that the mechanisms of mineral-induced diseases are not only related to morphology but are also related to other mineralogical properties. In addition, different mineral species may elicit different biological responses and, hence, may have different modes of action. Indeed erionite appears to activate different biochemical pathways from amphibole asbestos. For example, crocidolite asbestos (the amphibole riebeckite) induces two early proto-oncogenes (c-fos and c-jun) and so may induce cancer via this biochemical pathway. However, Na-exchanged erionite induced c-fos at comparable levels to crocidolite but c-jun at higher levels. In addition, crocidolite induces apoptosis (programmed cell death) in cells whereas erionite did not. These observations suggest that mineralogical properties (e.g., cation exchange characteristics, surface acidity) must be evaluated with respect to the potential health consequences of a mineral.

FORMATION MECHANISM OF ALTERATION MINERALS IN THE FRACTURES IN GRANITIC ROCK AT ASHIO, CENTRAL JAPAN

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Alteration minerals from a drill-core (maximum depth 2002 m) in the granitic rock at Ashio, central Japan, were studied by optical microscopy, X-ray diffractometry and analytical scanning electron microscopy. In the host rock, biotite is altered to chlorite and plagioclase to illite. Calcite has precipitated in veinlets and grain boundaries. The host rock close to fractures is strongly altered, whereas the rocks distant from fractures are less altered. Quartz, illite, chlorite, laumontite and calcite have precipitated on fracture wall. The alteration minerals are estimated to have formed in the range 140-200C, higher than the present temperature (13-96 C). The chemical composition of the ground water in the granitic rock at Ashio was estimated thermodynamically from the mineral assemblage. The alteration reaction of plagioclase and the precipitation of calcite may occur simultaneously. The alteration minerals formed in the host rock and in the fractures may adsorb radionuclides effectively, and thus may inhibit radionuclide transport to biosphere.

REDUCTION OF NITRATE TO AMMONIUM BY CARBONATE GREEN RUST

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Green rusts (GR) are layered hydroxides with general composition [FeII6-xFe IIIx(OH)12]x+, [Ax/n yH2O]x-, where 1.2<x<4.2, y=4 and A is an n-valent anion. GRs have mainly been identified as corrosion products of iron; but also may form during reductive iron(III) oxide dissolution in non-acid, anaerobic soils and sediments. Sulphate and carbonate anionic forms are expected to be the most ubiquitous in Nature. Sulphate-GR reacts with nitrate at pH 8 under the stoichiometric formation of ammonium and magnetite (Hansen et al., 1996), with the nitrate reduction apparently at interlayer sites close to GR particle edges. This work investigated the rate of nitrate reduction by carbonate-GR. Carbonate-GRs were synthesized at pH 7 by air oxidation of FeCl2 solutions using Na2CO3 as the neutralizing agent. The GR product was purified under argon and subsequently reacted with different concentrations of NaNO3at pH 8 and 25oC. The reaction was monitored by measuring Fe(II) in GR, nitrate and ammonium as a function of time. Mössbauer-spectroscopy of the initial GR products gave x=2, corresponding to the composition FeII4FeIII2(OH)12CO3. The final iron-containing product was identified as magnetite. The reaction with nitrate was close to the stoichiometry. At pH 8 the reaction was first order with respect to both Fe(II) in GR and nitrate, where k=5.25x10-5 L.mol-1s-1. The reaction is similar to the reaction between nitrate and the sulphate-GR, and thus both carbonate and sulphate forms of GR may be important as abiotic nitrate-reducers in anoxic environments.

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DIRECT BREAKDOWN OF CHLORITES FROM SILT TO FINE CLAY IN A GLEYIC PODZOLUVISOL OF THE PARIS BASIN, FRANCE

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Silt and clay fractions of a gleyic podzoluvisol of the Paris basin were studied by XRD, TEM, and total chemical analysis in order to estimate the chlorite contents in the different particle size fractions of the different horizons. XRD on air-dried specimens showed increase intensity of chlorite reflections from depth to surface horizons in coarse fractions (> 10 µm). The 2-5 Ám particle size fraction exhibited an inverse evolution with depth. TEM micrographs of chlorites of E Horizons showed particles of quite rectangular sections composed of numerous square particles, 50 to 100 nm sized, separated by voids of identical size. These results were interpretated as the beginning of small particles forming, by physical breakdown from a particle about ten times larger. Chemical variations of MgO contents of the

particle size fractions confirmed this physical evolution by a large increase in MgO of the fine clay fraction, chlorite being the sole mineral containing Mg in this soil.
Finally chlorite minerals were identified in the 0-0.2 µm fraction, on the XRD traces of samples previously heated to 550 C. The complex peaks between 1.0 and 1.4 nm were decomposed into elementary peaks. This showed an increase in the 1.4 nm peak intensity from depth to the surface horizon and a shift of equidistance of interstratified chlorite-smectite toward the low angles, showing an increase in chlorite and a change in the interstratified mineral constitution respectively. These results mainly involved a direct breakdown of chlorites from 2-5 µm to 0-0.2 µm fraction. They also involved a superimposed chemical weathering of the 2-5 µm fraction particles.

THE APPLICATION OF CLAY MINERAL STUDIES OF SEDIMENTS IN THE SANTA BARBARA BASIN TO PALEOCLIMATE STUDIES IN SOUTHERN CALIFORNIA

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Conspicuous gray, clay-rich sediments within the varved record of Late Holocene sedimentation in the central Santa Barbara Basin (SBB) were analyzed by particle size analysis, X-ray diffraction analysis and methylene blue adsorption. The SBB has a restricted source of sediments, predominantly from the Santa Clara and Ventura rivers. The study confirmed the presence of significant quantities of smectite within specific annual layers while adjacent layers had much lower smectite contents. The layers containing high smectite contents (approximately 20% smectite) have been interpreted to indicate years of extreme precipitation. Dates interpreted from these high smectite events were tightly correlated with other regional paleoclimatic evidence including tree-ring data, pollen data from lake and marsh cores and carbon isotope studies. Independent studies by Drake et al.(1971) of mineral compositions of suspended loads in the Santa Clara and other California rivers during recent (1989) flood events also showed similarly high levels of smectite during these events. Such clay mineral studies of restricted basin sediments may be applicable to paleoclimate studies elsewhere in the world.

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POSSIBLE DISCRIMINATION BETWEEN D- AND L-ALANINE DIMERS BY ALLOPHANE

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The possibility that clays can discriminate between optical isomers of amino acids has attracted much attention1. However, since layer silicates are not chiral they would not be expected to prefer one enantiomer to another2. Nevertheless, we have recently found that some soil allophanes could adsorb more L- than D-alanine3.
Here we report on the adsorption of D-and L-alanine dimers by two allophanes from Japan, and one from New Zealand. Adsorption isotherms were obtained by equilibrating air -dry allophane with solutions of either D- or L-alanine dimers at pH 6, centrifuging, and measuring the dimer concentration in the supernatant with a Simadzu TOC-5000 analyzer. The D/L ration of alanine dimers adsorbed by Kanuma (Al/Si=1.4), Kitakami (Al/Si=1.5), and Te Kuiti (Al/Si=1.6) allophanes was 0.999, 0.987, 0.913, respectively. Only the most aluminous Te Kuiti sample shows a clear preference for the L-enantiomer, suggesting that selective capacity

depends on composition. This observation may relate to the occurrence of structural defects (perforations) within the wall of allophane spherules where (OH)Al(H2O) groups are exposed. At the molecular scale these groups may conceivably serves as chiral (asymmetric) centres.

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CLAY DIAGENESIS IN A SANDSTONE RESERVOIR (MIDDLE JURASSIC) OF THE NORTH SEA

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The nature, composition, and relative abundance of clay minerals in sandstones of the Brent group have been studied. The sandstones have been sampled between 3200 and 3300 m in a well of the Ellon field (Alwyn área, North Sea). The well shows a heterogeneous calcite cementation of the sandstones. This cementation occurs during early-diagenesis. Clay diagenesis of the cemented and uncemented sandstones has been compared using the optical microscope, the SEM, XRD and infrared spectroscopy. Detrital illite and authigenic kaolinite are present in both cemented and uncemented sandstones suggesting that kaolinite precipited before calcite cementation. In uncemented sandstones, dickite replaces vermiform kaolinite with increasing depth. At 3205 m depth, illite replaces kaolinite and shows a progressive evolution of its morphology (fibrous to lath-shape transition). At 3260 m depth illite present a crystal isometric-shape whereas the kaolin minerals disappear. In cemented samples, vermicular kaolinite is preserved at all depths suggesting that dickite transformation has been inhibited by the presence of the calcite cement. This observation suggests that calcite cement would prevent fluid circulation and dissolution-precipitation reactions. Influence of cementation on clay neoformation is demonstrated in this study.

ELECTROKINETIC REMEDIATION OF CLAYS

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In Germany electrokinetic remediation is a coming up in situ technology for the clean up of fine grained sediments. For the first time electroosmotic processes offer the possibility for a directed transport of organic pollutants and heavy metals in contaminated clays. Materials: Different proctor-compacted clays, single dominated by one of the common clay minerals and a loess loam from Germany were investigated. Chromium, in the form of anionic chromate, and phenol were selected as representatives of heavy metal and semipolar organic contaminants. Methods: Electroosmotic permeability and contaminant transport were evaluated using computer automated electrokinetic percolation cells. After remediation, the soil cores were analysed for CEC, specific surface área, pH, mineralogy and soil mechanical parameters. Contaminations were quantified by atom adsorption spectrometry, gas chromatography and the phenol-index. Results: The mass balance of phenol remained in the clays after electrokinetic treatment and phenol collected in the percolate showed unexpected results. As known from the literature kaoline shows the best removal efficiency. In comparison only 12% of the initial amount of phenol could be collected in the percolate of the illitic clay and no more than 4% from the loess loam, but only 15% respectively 5% could be detected after a posttreatment chemical extraction of the clay matrix. Different voltages applied on the soil samples led to important changes in the direction of chromate transport. The results show that the clay mineral composition controles the electroosmotic permeability, removal efficiency, and transport mechanism of the electrokinetic remediation technology in fine grained sediments.

ARTIFICIAL TRANSFORMATION OF NATURAL SEPIOLITE INTO Ni-, Co- AND Cu-SEPIOLITE

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Sepiolite is a fibrous hydrous magnesium silicate with intramolecular tunnels along the fiber axis and the Mg 2+ along the tunnel wall which can be substituted with transition metal ions. The substitution reactions of the Mg2+ in sepiolite samples were carried out following 2 methods: 1) After artificial transformation of sepiolite into loughlinite, it was added in 0.1 N nickel, cobalt and copper acetate solutions at 25 C or 75 C; 2) An original sepiolite was heated at 200C, 400C, 600C and 700C for 4 hours prior to action exchange manipulation. The heated sepiolite was added 0.1 N nickel, cobalt and copper acetate solutions at 25C or 75C. The products of both methods were centrifuged, washed repeatedly with deionized water and air-dried overnight at 60C. In the case of method 1, Mg 2+ along the tunnel wall of sepiolite was substituted by Na nearly completely for 8 hr at 75C. Increasing the reaction time, Ni treated samples tend to be became greenish (decrease in a* value in color space). The reaction rate increased with increase of reaction time at 75 C. The Ni ions incorporated for Mg ions in sepiolite exist in the divalent state and are octahedrally-coordinated. In the case of method 2, the high substitution rate was yielded by the samples heated at 400C for 4 hours. These results suggested that Mg2+ ions in sepiolite are substituted by Ni, Co and Cu ions easily.

LOCATIONS AND DYNAMICS OF INTERLAYER CATION AND WATER IN KANEMITE

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The locations and dynamics of interlayer sodium (Na) cation and water in kanemite have been studied by means of solid-state 1H, 29Si and 23Na NMR. In addition to one-dimensional (1D) spectra, 1H-29Si two-dimensional (2D) cross-polarization (CP) correlation, 23Na 2D nutation and 23Na 2D triple-quantum spectra were also measured. Hydroxyl groups have a large 1H chemical shift (15 ppm), forming strong hydrogen bonds of the Si-O-H--O-Si type between the layers. When the amount of the water is large, the water molecules are mobile in the interlayer space. With decrease in the water content, the motion of the waters is restricted. There is only one Si site in undried kanemite. The decrease in the water content affects the layer structure, which is indicated by a new 29Si peak. The dominant species of Na ions have a chemical shift of 2.9 ppm, a quadrupole coupling constant of 2.05 MHz and an asymmetry factor of 0.63. The Na ion does not rotate isotropically, but has a fixed position. Water molecules do not coordinate to the Na ions directly. A part of Na ions are hydrated and undergo isotropic motions in the undried sample. With decrease in the water content, these Na ions are dehydrated, and their motions are restricted.

MECHANISMS OF PHOSPHORUS RETENTION BY SANDY PODZOLS ON THE SWAN COASTAL PLAIN OF SOUTHWESTERN AUSTRALIA

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Eutrophication of waterways is a worldwide environmental issue in áreas affected by agricultural and urban run-off. The Swan Coastal Plain in Western Australia (WA) contains 85% of WA's population. Algal blooms caused by the rich supply of nutrients, particularly phosphorus (P) in the Peel-Harvey Estuary and other *waterways developed as public and scientific concerns in the 1970s. About 90% of P enters these waterways in drainage water from the very sandy soils of the coastal plain which are used for pasture and receive annual P application. The present study was designed to (I) investigate the seasonal dynamic of P mobility in the soils and its relation to soil properties, and (ii) develop the results into a management strategyfor P contamination control. 16 samples of deep sandy podzols were collected from 3 soil profiles representing major soil types. P sorption and desorption isotherms were obtained for wet (field condition) and air-dried samples. 10 samples have very low P sorption capacities with Langmuir maximum sorption capacities (LM) of 0.7 to 7.9 mg/kg soil. Differences in P sorption associated with drying are negligible. 6 samples show larger LM ranging from 50 to 500 mg/kg. Air-dried samples show higher LM than corresponding wet samples with LM increasing from 21% to 111%. There are significant positive relationships between LM and amounts of pyrophosphate, oxalate or dithionite extractable aluminum in these soils but no relationship between LM and organic carbon, extractable Fe and clay content. These results provide a basis for developing improved fertilizer use practices.*

CAL MODULE: XRD IDENTIFICATION OF CLAY MINERALS

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This Windows based interactive computer assisted learning (CAL) module teaches step by step clay mineral identification by X-ray diffraction (XRD). Individual XRD traces of matching species of all eight clay mineral groups and most of the subgroups are presented. The first part of the module is instructional. It highlights diagnostic features in patterns of oriented clay preparations in the air dry state and after various treatments (ethylene glycol, hydrazine, 500C). Emphasis is placed on the appropriate sequence of treatments required to distinguish between minerals with overlapping peaks in their natural state, namely the 14 and 7 phyllosilicates. The second part of the module demands interactive participation by the student. It provides clay material traces for evaluation and requires the student to propose an identification. These patterns appear in a random fashion but with an increasingly complex nature. Throughout this session appropriate responses are given and the student is able to review parts of the instructional section. A printable set of notes is included with this CAL module.

DIAGENESIS IN AN ECONOMIC DEPOSIT OF FULLER'S EARTH: EVIDENCE FROM SILICA PHASES

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Palygorskite and smectite comprise the major sorptive minerals of an economically significant Fuller's earth deposit from south Georgia, USA. Accessory components including quartz, chert, and opaline and amorphous silica affect the utility of the mined clay deposit for diverse applications. The various silica phases represent both detrital and primary occurrences, thus serving as important determinants for the genetic and diagenetic history of the deposit. The occurrence of the different silica phases, notably microcrystalline and opaline silica, are examined particulary relative to solution features and oxidative weathering sequences. X-ray diffraction methodologies are developed to relate phase identification to textural evidence from optical and scanning electron microscopy, and these data are integrated with chemical analysis from electron microprobe studies. Such an approach correlates the silica phase occurrences to assumptions regarding silica mibility *within the deposit. Diagenesis of the clay mineral sequence is interpreted in terms of the geochemical regime indicated by the transport and reapportioning of silica.*

Textural and chemical evidence from the silica phases, and from their relationship to the clay mineral components, can also be interpreted in terms of the utility of this mineral deposit in sorptive and specialty applications. The quantitative measurement of various silica phases in the deposit is crucial to exploration and beneficiation efforts, as well as regulatory compliance, for the mined deposit. Accurate analysis of crystalline silica content necessarily includes differentiation of the regulated crystalline species, which can be complicated by the characterization of opaline phases present.

RECONSTRUCTION OF ARCHAEOLOGICAL CLAY SOURCES USING APPLIED CLAY MINERALOGY TECHNIQUES

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Lerna, a prehistoric site in the Argolid, Greece, displays a well-stratified sequence from the Final Neolithic (ca. 4000-3000 B.C.) through the Early Helladic III (ca. 2300-2150 B.C.) period. Significant ceramic technological changes occurred at Lerna over the course of the Third Millennium; however, previous studies have emphasized stylistic changes in the ceramic artifacts. This study examines assumptions about cultural change in light of clay-mineralogical analysis, including X-ray diffraction (XRD) and electron microprobe (EMP), of ceramic artifacts and local source clay-sediments. A reconnaissance project using EMP examined Lerna ceramic artifacts relative to a suite of heavy mineral grains from local clay-rich sediments. Matrix clay composition in two of the four major Lerna petrographic groups was linked to a hypothetical mixed-layered illite/smectite. The Lerna ceramics from these two groups appear to be low-fired, as there is no visible alteration of matrix muscovite in the ceramics. XRD analysis of archaeological ceramics has not received adequate attention from archaeological researchers; scarce methodologies customized to the small sample size and optimal retrieval of intact clay minerals from the sherds restrict this approach. Precision and standardization of techniques applied to these ceramics would enhance interpretation of ancient clay sources and firing temperatures. Results from various XRD mounting and analytical techniques for small amounts of Lerna ceramic materials will be presented and integrated with the EMP analysis of matrix clay composition.

A SLOW-RELEASE FORMULATION FOR HERBICIDES: ORGANOCLAY-FENURON

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The organic chemicals adsorb in organoclays by hydrophobic bonds to the alkyl chains of the organic interlayer cations, but some polar interactions are also shown to contribute in the case of organic polar compounds. These two bonding types make organoclays good candidate as slow-release carriers of herbicides to be added to soil and water. The aim of this work was to assess the sorption capacity of different organoclays for the herbicide fenuron and the effect of supporting it on the organoclay in the leaching of this herbicide through a sandy-clay soil. The organoclay sorption capacity for fenuron was obtained from the adsorption isotherms by the Freundlich equation. The fenuron-organoclay complex was prepared by mixing the selected clay with a methanol solution of the herbicide to result in 2% and 4% fenuron content. These complexes and the pure herbicide were applied to a hand-packed soil column and the herbicide leachates concentration measured after a 50 ml water daily application. The sorption isotherms shapes and parameters show the organoclay as good sorbent for fenuron and suggest the hydrophobic interaction as the main bonding mechanism. The soil leachate concentrations of the herbicide from fenuron-organoclay (2 and 4%) decreased up to 1/3 and 1/2 of those corresponding to the pure fenuron. These preliminary results suggest the possible use of organoclay-herbicide association as slow-release formulation to minimize the environmental adverse effects of these agrochemicals. This work has been financed by CICYT Project AMB96-0445-CO2-01 and PAI Research Group 4092.

ORGANOHYDROTALCITE AS SORBENT FOR PESTICIDES

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Hydrotalcites (HT) are antitypes of clay minerals:brucite layers with Al-for-Mg subtitution imparting positive layer charge compensated by inorganic interlayer anions easily exchangeabe. The inorganic anions can be substituted by large organic ones giving the lipophilic character to hydrotalcite (organo hydrotalcite, OHT). The aim of this work is to assess the potential sorption capacity of OHT for two pesticide compounds: metalaxyl and chloridazon in looking for two possible OHT uses as sorbent for pesticide contaminated waters or as carrier for pesticides in slow release formulation. The interlayer CO3= anions of the hydrotalcite (HT) [Mg3Al(OH)8]2CO3were exchanged by those of dodecylsulphate (DDC) by the reconstruction method, suspending 1g of the HT calcined product (2h, 500°C) (HT500) in DDC 17mM. The pesticide adsorption on OHT was measured by batch equilibration technique at diverse pH, contact time and DDC concentration. The suspensions were shaken and after 24h the supernatants were filtred to determine the pesticide concentration by UV-absorbance. The results suggest that the amount of metalaxyl removed by OHT were much higher than that of chloridazone. The attractive effect between the negative charge of sulphate and protonated form of the metalaxyl besides the lipophylic alkyl chains interactions facilitate the penetrance of the contaminant into the interlayer of OHT enhancing adsorption. The lower sorption of cloridazone is probably because of the absence of the alkyl chains in its structure.

THERMAL DECOMPOSITION AND RECONSTRUCTION OF HYDROTALCITE-LIKE COMPOUNDS

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Reconstruction of hydrotalcite-like compounds (HTlcs) has been reported to be a facile method of intercalating various anions. Calcined and decarbonated Mg-Al-CO3HTlcs can be reconstructed to HTlcs structure in aqueous solutions. We studied thermal decomposition of Mg-Al-CO3 HTlcs and reconstructed HTlcs to understand further the processes occurring during reconstruction. The present work demonstrates that 20-30% of the carbonate anions remained when Mg-Al-CO3 HTlc having maximum Al content (Mg/Al=2/1) were heated to 500°C, although the decarbonation has been thought to occur at about 400°C. The remaining carbonate anions were evolved as Al ions migrated in the oxide at 600°C and 900°C. We speculated that collapse of the layer structure (350°C) just before main decarbonation (380°C) disturbed the evolution of carbonates. Therefore, carbon-hydrotalcite complexes that were Mg-Al-CO3 HTlcs containing carbon residues and carbonate anions in their interlayer galleries were prepared from HTlcs containing organic anions by reconstruction method. The carbon-hydrotalcite complexes increased their thermal stability of layer structure by about 100°C as compared with Mg-Al-CO3 HTlc, and the decarbonation occurred very sharply at 380°C. However some carbonate anions still remained after the main decarbonation. During the study of preparation of carbon-hydrotalcite complexes, it was noted that HTlcs reconstructed under particular conditions yielded spinel at a low temperature (400°C), as a side reaction between edges of crystallites. The conditions were that crystallites of starting HTlcs coagulated tightly and that samples were not ground during reconstruction process. The evidence suggests that reconstruction of HTlcs is a more complicated reaction than was previously thought.

SYNTHETIC HECTORITE: A REGULARLY ORDERED INTERSTRATIFICATION DUE TO UNUSUAL HYDRATION

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A regularly interstratified hectorite has been synthesized from the starting slurry comprising 0.5 wt% hectorite composition prepared at a ratio of Na:Li:Mg:Si = 0.5:0.5:2.5:4.0, when hydrothermally treated at 300 C for 2 hours. Its XRD data are given as follows:

RH(%)	0	20	40	60	80	100	EG
d001(Å)	?	23.2	23.9	24.5	25.9	30<	17.7
d002(Å)	11.0	11.4	11.7	12.8	13.8	?	8.7

This specimen is characterized by a long spacing reflection of 23-26Å accompanied with its nearly rational 2nd reflection under the relative humidity (RH) condition of 20-80%, which is suggestion of nearly 1:1 ordered interstratification of two differently hydrated hectorite components. When treated with ethylene glycol (EG), however, this material contracts to 17.7Å like the usual (not interstratified) hectorite, indicating the interlayer is no longer discriminative but uniform. Calculated XRD simulation considering the other higher order reflections also reveals predominant alternation of the 0(anhydrated)/l water layer components and the 0/2 water layer components under the RH range of 20-40% and 60-80%, respectively. Paired coexistence of different hydration states in the hectorite structure throughout the RH range is noted to be extraordinary. Total exchangeable cations of this specimen is 66 meq/100g, which is excessively low as compared to 134 meq/100 g of the usual hectorite. Structural and/or compositional polarity, e.g. alternate distribution of the fixed and exchangeable cations in the interlayer of the hectorite, if assumed, could stabilize such regularly ordered interstratification.

HIGH-GRADIENT MAGNETIC SEPARATION OF CLAY MINERALS: THEORY AND PRACTICE

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The potential of high gradient magnetic separation (HGMS) as a technique for the laboratory separation of clay minerals has been recognised for almost thirty years. In that time HGMS has been applied with varying degrees of success to mixtures of clay minerals from various kinds of samples. In all cases, the conditions used are either chosen arbitrarily or determined on a trial and error basis. However, the physics of HGMS have been the subject of intensive research and it can be shown that, if the size of the particles and their magnetic susceptibility are known, the conditions necessary for capture of particles in an HGMS system can be defined in terms of the ratio of the velocity of the particle slurry (Vo) to the magnetic velocity (Vm). The use of the theory to pre-determine the conditions necessary to separate minerals has been investigated by comparison with the results of applying HGMS to artificial binary mixtures of three clay minerals. The minerals used are illite, chlorite, and kaolinite separated into different size fractions. The magnetic susceptibilities of the minerals have been both measured and calculated from chemical analyses. Problems such as mechanical trapping and aspects of the design of laboratory HGMS systems will also be considered.

EXPERIMENTAL WEATHERING OF MICAS UNDER LEACHING CONDITIONS IN THE PRESENCE OR ABSENCE OF RYEGRASS

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The direct implication of plants in the weathering of micas has already been demonstrated by mineralogical investigations of the rhizosphere in laboratory experiments (Leyval and Berthelin, 1991; Hinsinger et al., 1993) and even field experiments (Kodama et al., 1994). However, the effect of plants on the rates of weathering of silicates is still a question for debate (Drever, 1994). In the present experiment, 50 mg of silt-sized mica contained in a dialysis bag was leached at a flow rate of 25 cm3 day-1 with a potassium-free nutrient solution for fourteen days. In another treatment ryegrass was grown on top of the mica bags under the same leaching conditions. Three micas were compared: biotite, phlogopite and muscovite. The analysis of the leachates and plants provided an estimate of the mica dissolution rates. Exchangeable cations, cation exchange capacity (CEC), elemental composition and x-ray diffraction (XRD) patterns of the micas were also measured. Only minor changes in chemical properties of the micas were obtained in the absence of plants: CEC slightly increased but no mineralogical change was detectable by XRD. Conversely, in the presence of ryegrass, CEC increased significantly for biotite and phlogopite and XRD revealed a substantial transformation into vermiculite. In the presence of plants 25-35% of potassium was released from trioctahedral micas. This represents a five to six-fold increase in the dissolution rate in the presence of ryegrass. For muscovite, a minor increase in the dissolution rate was obtained. The chemical interactions between micas and plant roots are further discussed.

ROOT-INDUCED DISSOLUTION OF A SYNTHETIC GOETHITE IN THE RHIZOSPHERE OF HIGHER PLANTS

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Due to the low solubility of iron oxyhydroxides, Fe concentrations in soil solutions are always smaller than the concentrations required for adequate plant nutrition (Lindsay, 1974). In spite of such adverse conditions, higher plants can meet their Fe requirements through various strategies, as evidenced by plant physiologists: (i) proton excretion, (ii) root-enzyme catalysed reduction and (iii) exudation of complexing substances (Römheld, 1987). However, in these experiments Fe was not supplied as Fe-bearing minerals. There is thus a need for verifying to what extent plants can solubilize iron oxyhydroxides, that is the most ubiquitous source of Fe for plants. In the present experiment, the only source of Fe for plants was a synthetic goethite. Four species (canola, lupin, maize and pea) were studied with a cropping technique that physically separates the roots from the goethite (Hinsinger and Gilkes, 1995). In such conditions, Fe solubilization can be deduced from the analysis of the whole plants. All four species solubilized significant amounts of Fe from the goethite. The corresponding rate of dissolution ranged between 30 to 200 ng h-1 m-2. This is fairly high compared with the data reported by Schwertmann (1991) for the abiotic dissolution of goethite in 0.5M HCl which was 1000 ng h-1 m-2. The analysis of rhizosphere material showed that in the presence of plants (i) pH decreased systematically and (ii) in all cases but for maize, oxalate- and DTPA-extractable Fe increased. Such an increase in the bioavalailability of Fe from goethtite in the rhizosphere is further discussed.

EARLY MARINE AUTHIGENESIS OF K- AND Mg-RICH SMECTITE IN A HYPERSALINE TIDAL FLAT, SALINA OMETEPEC, MEXICO

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Sediments, overlying water, and pore waters were sampled via push-cores and peepers along a 5 km transect across the hypersaline Salina Ometepec tidal flat to determine the earliest changes in smectite composition during interaction with marine derived brines. Solid phases were characterized by XRD and STEM/AEM. Major and minor ions were determined in overlying and pore waters. Tidal-flat overlying and pore water salinities reflect the 10-fold evapoconcentration of seawater and redissolution of halite from upper sediment layers. Tidal flat pore waters have exceptionally high Mg2+ due to gypsum formation, which favors sediment Mg2+-uptake. AEM analyses of smectite show K+ is the dominant interlayer cation. Detrital smectite from the normal marine setting is dioctahedral: K0.7(Al3.3Fe3+0.3Mg0.5)(Al0.7Si7.3)O20(OH)4. Smectite from the hypersaline setting is K-rich saponite containing significantly more Mg2+ than normal marine clays: K0.7(Al0.7Fe3+0.5Mg4.45)(Al1.16Si6.84)O20(OH)4. STEM images show such smectite crystallites are <250nm, euhedral, and pseudo-hexagonal plate- or lath-shaped. Electron diffraction patterns are consistent with turbostratic rotations of small coherent domains about c*. Lattice fringe images of smectite show layers are irregular and wavy with interplanar spacings of 11 to 13Å. Individual crystallites are as small as 2-3 layers. The euhedral Mg-rich smectite in hypersaline sediments is inferred to be authigenic and derived through alteration of detrital dioctahedral smectite. Such Mg-smectite may serve as the precursor for trioctahedral mixed-layer smectite, corrensite, and chlorite assemblages characteristic of ancient marine evaporative sequences. This study supports accumulating evidence that interlayer K+ in smectite from marine settings has its origin during very early diagenesis near the sediment-water interface.

SEPARATION OF HALLOYSITE FROM BULK SOIL MATERIAL FOR OXYGEN ISOTOPIC ANALYSIS

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Soil is a heterogeneous mix of organic matter, and primary and secondary minerals. Isolation of monomineralic samples of halloysite from soils in Hawaii through chemical dissolutions of grain coatings as well as physical separations are described. Because the d18O value of halloysite could be affected during chemical treatments, its resistance to isotopic exchange during those treatments was also investigated. Organic matter is first removed by oxidation with 30% H2O2 (Jackson, 1979). Non-crystalline (amorphous) iron and aluminum components are removed using an acid ammonium oxalate solution (McKeague and Day, 1966) and crystalline iron oxide coatings such as goethite are removed using a citrate-bicarbonate-dithionite extraction (Jackson, 1979). The latter two treatments were repeated alternately until there was sufficient clean clay material for physical separations. Initial size separations of the clay material were made at 5 and 2 microns, and the mineralogy of each fraction was determined by x-ray diffraction. Further size separations of mixtures were made on the < 2 micron fraction, guided by measurement of the particle size distribution using a Nicomp Model 370 Submicron Particle Sizer. Size separations were terminated when halloysite was the only mineral identified by x-ray diffraction. This approach was successful for most samples. Chemical treatments were repeated on the cleaned halloysite sample using isotopically labelled water (d18O=+300). Only about 1% of the total oxygen in halloysite was exchanged during the treatments. Thus, the chemical purification of *halloysite using solutions made with laboratory distilled water does not measurably affect the oxygen isotopic composition of halloysite.*

MECHANISM OF KAOLINITE DISSOLUTION AT ROOM TEMPERATURE AND PRESSURE

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Kaolinite dissolution experiments were carried out in batch reactors over 450 days, under the following conditions: 25oC, pH range 1-13, 1M ionic strength.

Steady-state dissolution was reached after an initial reaction period of ~600 h. Steady-state dissolution was congruent at pH<4 and pH>11. Experiment with Al-complexing agents and thermodynamic considerations indicate that the incongruent dissolution observed between pH 5-10 is due to the precipitation of gibbsite.

The overall reaction at each pH was modelled taking into account the initial and steady-state processes. According to the surface coordination chemistry, the dissolution rate is proportional to the concentration of surface complexes due to the protonation and deprotonation of the kaolinite surface. The combination of the pH-dependent dissolution rates and the surface speciation allowed one to evaluate the contribution of the different complexes to the dissolution mechanism. The calculated equation provided a very good description of the overall rates (mol/m2s):

Rate = 10-8.43[Al2OH2+]ext + 10-10.9[Al2OH2+]int0.5 + 10-8.7[Al2OH+SiOH] + 103.8[Al2O-]3

The dissolution mechanism is thus controlled by the charged surface complexes at the external and internal Al2OH sites and to a small extent by the neutral Al2OH and SiOH sites. No contribution was observed for the SiO- complexes. In addition, this rate law predicts a minimum of the dissolution rate, which is observed at pH~9.

SILURIAN K-BENTONITES OF PODOLIA, UKRAINE

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The Dnestr Basin of Podolia, Ukraine, is a marginal basin consisting of neritic, carbonate and carbonate mud facies ranging from late Llandovery to late Pridoli in age. It has served as a standard for regional and interregional studies due to its well documented macro and microfaunal assemblages. In addition, numerous (24) K-bentonites occur which are laterally persistent and have aided in establishing regional correlations. The K-bentonites range from 1-40 cm in thickness and occur in the Bagovitsa (late Wenlock), Malinovtsy (Ludlow) and Skala (Pridoli) Formations. While lateral tracing of the K-bentonites has been accomplished using biostratigraphic criteria, little is known of the mineralogical and geochemical characteristics of these beds. Such features are important not only for determining the tectonic setting of the source vents but also for high-resolution correlation of individual beds. Like many lower Paleozoic K-bentonites these beds consist dominantly of mixed-layer illite/smectite (I/S) with some traces of discrete illite. Unlike Silurian K-bentonites elsewhere, however, kaolinite is lacking as an accessory phase.

Furthermore, the I/S varies in a non-systematic way from R0 to R3 ordering over a stratigraphic range of some 200 m. R3 ordered I/S occurs mainly in the mud-dominated Skala Formation, while R0 through R2 ordered phases occur in the carbonate rich Wenlock and Ludlow strata. The Silurian section in Podolia has not been subjected to any significant deep burial in its history and it appears the I/S ordering and associated distribution of alkalis are mainly controlled by facies composition rather than burial metamorphism.

SOME MINERALOGICAL AND CERAMIC CHARACTERISTICS OF POTTERY CLAYS IN SOUTH AFRICA

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Despite the production of pottery in South Africa for centuries, relationships between the mineralogical and ceramic properties of the clays are not clearly understood. As part of a student practical in clay mineralogy, X-ray diffraction (XRD), infra-red, differential thermal analysis (DTA) and electron microscopy were used to examine the mineralogy of a studio clay, a porcelain clay, and a terracotta clay, all produced commercially, and a traditional Zulu pottery clay from KwaNyavu, KwaZulu-Natal. All the clays have kaolinite as the main component but its degree of crystallinity varies, from the highly crystalline porcelain to the poorly ordered KwaNyavu deposits. Subsidiary minerals in most of the clays are muscovite, K-feldspar and quartz. Goethite gives the terracotta clay its valued red burning property. The porcelain contains a small amount ofmontmorillonite; the KwaNyavu clay a substantial amount of vermiculite. The KwaNyavu clay is a mixture of three local clays (red, black and yellow) and is shown to consist mainly of the yellowclay with small amounts of the red and black clays added. The studio clay has excellent versatility and is used for both earthenware and stoneware. The porcelain clay mix is used when translucency in the final product is required. The kaolin in this mixture is Serina kaolin, the only South African deposit of sufficient purity, which is shown to be the source of the muscovite and K-feldspar in the porcelain clay.
The mineralogical variation of the clays is related to the particular ceramic wares produced.

SEQUENTIAL DISSOLUTION OF CLAY MINERALS II: TRACKING STRUCTURAL COMPOSITION

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A recently developed sequential dissolution-ICP-XRD method gives cation measures of individual clay minerals in mixtures. Heating allows extraction sequentially of clay minerals with higher dehydroxylation temperatures. Samples are extracted in 2N HCl and centrifuged for ICP or AA analysis of liquids and XRD of solids.
XRD results show which samples to submit for ICP. Unexpected results include the purification of smectitic layers from partially dehydroxylated mixed-layered kaolinite/expandables (K/E or K/S) and formation of expandable layers from high-iron illite and Mg-rich diagenetic chlorite- most illites are insoluble and Mg-Fe and Fe-rich chlorites show coherent dissolution. Lithium anomalies were found in berthierine-containing flint clays and in a fireclay. Addition of this lithium to structural formulas for these berthierines eliminates octahedral voids that were required previously for charge balance (Brindley, 1982, Clays and Clay Minerals, V. 30, 153-155). Also, dissolution of mixed-layered 7Å chlorites suggests that the 7Å layer is berthierine-like. Cations are dissolved with three general trends: 1)during first 16 hours or so, AlVI tracks octahedral cations, while later expression of AlIV tracks Si with its slower dissolution rate; 2) brucite and 10Å-layer octahedral cations in diagenetic chlorites dissolve at the same rate for Mg-Fe and Fe-rich chlorites, while brucite sheets dissolve faster for Mg-rich samples, producing a metastable vermiculite by product; and 3) tetrahedral Si and Al in berthierines from flint clays dissolve faster than octahedral cations.

INFRARED (FTIR) SPECTROSCOPIC STUDY OF REDUCED AND REOXIDIZED Fe-SMECTITES

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Many studies have revealed profound changes in the physical and chemical properties of clay minerals by virtue of changes in the structural Fe oxidation state. This phenomenon is of great importance to the performance of minerals in agriculture, industry, engineering, and the environment. Changes in crystal structure have also been studied using infrared, Mössbauer, and optical spectroscopy, but the mechanism linking structural and physico-chemical properties has yet to be fully established. And little study has been done on the reoxidation of Fe-reduced clay minerals, which is crucial to understanding the long-term effects of redox cycles. The purpose of this study was to raise the level of understanding of chemical reduction and reoxidation mechanisms of Fe-rich smectites using Fourier transform infrared (FTIR) spectroscopy, covering a wide range of Fe(II) composition from unaltered (completely oxidized) to completely reduced, and the systematic reoxidation of reduced samples. The stretching and bending modes of O-H and Si-O were examined in four different Fe-rich smectites. Results revealed significant modifications in all regions of the FTIR spectrum for all samples, including a decrease in intensity and broadening of the O-H stretching band, accompanied by the appearance of a new, sharper peak at high wavenumber. Upon reoxidation the original band was only partially restored. Shifts in position and shape of the Si-O bands were alsoobserved. These results are consistent with a reorganization of the site occupancy of Fe in the octahedral sheet and changes in structural OH content of the smectite.

FLOCCULATION BEHAVIOR OF FOUR SYNTHETIC ORGANIC POLYMERS AND A SMECTITE CLAY

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These organic polymers which have been used as flocculants and aggregating agents were mixed with Na-montmorillonite (<2µm, freeze-dried) from Wyoming (SWy-2) in 500 ml batches containing 1 gram of clay. The polymers are a high molecular weight cationic polyacrylamide (494C) and an anionic polyacrylamide (836A), and a moderately low molecular weight cationic polymer (587C) and an anionic polymer (Aerotil L), all are marketed by CYTEC, Indianapolis. Each clay suspension series consisted of several polymer concentrations that were stirred and allowed to stand for 24 hours. After that the solutions were centrifuged and the clay plugs were washed and dried. Dried samples were investigated by XRD to determine properties of the treated smectite. The suspended clay containing anionic polymers was not flocculated at any concentrations of polymer. But the suspensions containing two cationic polymers were rapidly flocculated at almost all concentrations. The d(001) smectite spacings after they were treated with two cationic polymers produced 14.2-15.5Å peaks compared to the 12.8Å spacing of the polymer-free sample suggesting some polymers may have entered the interlayer spaces. The spacing in 587C polymer was higher than 494C. Cationic polymer treatment reduced glycerol expansion of smectite. The expansion of the smectite treated with 587C polymer was reduced more than that of 494C polymer. The above observations indicate that the moderately low molecular weight polymer (587C) was more apt to penetrate into interlayers of smectite than the high molecular weight polymer. Other investigations by CEC and IR are in progress.

SYNTHESIS AND PROPERTIES OF REGULARLY INTERSTRATIFIED LAYERED SILICATE HETEROSTRUCTURES.

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Randomly interstratified clays with segregated galleries may be obtained on partial exchange of inorganic cations by cationic surfactants. In these systems both *cationic species may also mix within galleries when the segregation process is not complete. Hence, the intercalation of diverse cationic species in clays does usually not lead to a spontaneous formation of clays with regularly interstratified segregated galleries. Heteroionic clay minerals with a regular arrangement of distinguishable galleries are rare. We have synthesized for the first time heterostructured clays with regularly interstratified segregated organic and inorganic galleries from smectite clays. Three different synthetic pathways were discovered that lead to the formation of these heterostructures. These one step processes include a pathway that involves ion-redistribution between homoionic parent end members. X-ray diffraction, thermogravimetric analysis, selective cation exchange and solvation experiments on the heterostructured clays verified the regularity of interstratification in addition to the gallery segregation. The hydrophilic nature of the inorganic galleries in addition to the hydrophobic character of the organic galleries generates new intercalation chemistry not provided by well known interstratified clay minerals. The heterostructured clays combine and preserve the properties associated with both individual intercalates through gallery segregation. Intercalation of different cationic surfactants allows for the fine tuning of the materials' properties.*

CRYSTAL CHEMISTRY OF NATURAL FERRIHYDRITES

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Poorly crystalline minerals or XRD-amorphous compounds are very reactive transient phases and are key materials for understanding the behavior of both major and minor elements at the Earth's surface. Among them, hydrated ferric oxides or ferrihydrites have been intensively studied from laboratory experiments, and structural models have been proposed for synthetic 2 and 6 lines ferrihydrites. On the contrary, little is known on natural ferrihydrites which frequently contain silicon and other minor elements. Due to their long range disorder, structural characterization of cation sites in XRD-amorphous materials cannot be studied by using classical X-ray scattering methods and their chemical complexity requires selective chemical probes. In the present study, structural data are reported for natural ferrihydrites, occurring in spring deposits and in weathering materials of volcanic rocks and granite. The study of these natural phases has been performed by using X-ray absorption spectroscopy at Fe-K edge at low temperature (10K). The derived structural data provide relevant information to determine: 1) the local and medium range structure of these short-range ordered phases. This structural information will be discussed as a function of the origin of the ferrihydrites studied, and of their chemical properties. For example, in Si-ferrihydrites originating from stream deposit (Guadeloupe) and from weathering of granite (Massif Central, France), the derived Fe-Fe distances indicate a predominance of edge-sharing octahedra as in 2 lines-ferrihydrite synthesized from Fe(II) path.

EFFECT OF HYDROXY-INTERLAYERED CLAY MINERALS ON HYDROQUINONE IN THE FORMATION OF HUMIC SUBSTANCES

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The formation of humic substances was studied in montmorillonite and montmorillonite with interlayered hydroxy-Fe, mixed hydroxy-Fe,Al, and hydroxy-Al.
Hydroxy-interlayered-hydroquinone (HIH) complexes were prepared by adding pre-weighed amounts of hydroquinone to the clay suspensions at two pH levels.
These suspensions were aged for 30 days in the dark and then filtered. The supernatant and HIH-complexes were analyzed for organic C fractions. Infrared and

XRD spectra of the solid HIH-complexes were also obtained. Humic acids separated from supernatant solutions were directly correlated to the darkening of hydroquinone as measured by the absorbance at 400 nm. The rate and degree of darkening varied with the kind of clay mineral, the stability of the hydroxy-interlayered material, and the pH of the system. Non-interlayered montmorillonite, having Na as the exchangeable cation contained the highest amount of humic acid C in supernatant, while hydroxy-Fe, and mixed hydroxy-Fe,Al yielded modest amounts. The most stable hydroxy-Al interlayered clay gave the least amount of humic acid C in the supernatant. These results were supported by K400, log K and RF values. Amounts of organic C retained by the clay were <2% of the added amounts. Varying amounts of C retained as HIH complexes are explained on the basis of specific surface área and the presence of positively charged functional groups. More than half of this adsorbed C was non-extractable in the alkaline solutions suggesting its contribution to the formation of stable organo-mineral complexes.

DO LEACHING EXPERIMENTS IN DEEP-SEA CLAYS ISOLATE A SEAWATER COMPONENT? INFERENCES FROM THE ATLANTIC AND INDIAN OCEANS

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Leaching experiments were carried out on the clay size fractions of deep-sea sediments from the central Indian Ocean and the northern North Atlantic. The behaviour of Sr and Nd isotopes during leaching was analyzed in sediments from the Indian Ocean whereas the Sm-Nd isotopic system was investigated in samples from the Atlantic. All leaching experiments modified drastically the geochemical signature of initial clays. Leachates from the Indian Ocean have Sr isotopic compositions similar to that of seawater, the residues being more radiogenic than the corresponding fine fractions. The Nd compositions are lower in the residues, suggesting that the Nd removed in the leachate might also derive from seawater. This indicates that this method has been very efficient to remove the seawater component, at least for Sr. In contrast, the conclusions drawn for Sm-Nd leaching of the clays from the North Atlantic are completely different. The residues display 147Sm/144Nd and 143Nd/144Nd ratios lower than corresponding fine fractions. Nd compositions of the leachates are surprisingly high, much more radiogenic than bottom waters and than corresponding fine fractions. In addition, the leachates display very high Sm and Nd concentrations, suggesting that the removed REE may be related to authigenic Fe-Mn oxides. These results indicate that the removed component does not display the Sm-Nd signature of seawater, but has undergone the influence of an oceanic crust, perhaps by the means of hydrothermal fluids.

IN-SITU GROWING KAOLINITE UNDER THE HYDROTHERMAL CONDITIONS OF OHYU-NUMA EXPLOSION CRATER LAKE, HOKKAIDO, JAPAN

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Ohyu-numa is an active explosion crater lake in southwest Hokkaido, Japan. Hydrothermal fluids are now discharging at a total rate of about 1,120l/min from several conduits of the lake bottom. The discharged fluids mix with inflowing cold river waters in the lake and these waters are balanced by outflow through river and evaporation from the lake surface. The temperatures of lake water are nearly constant in the upper parts to be about 40 C but increase steeply from a specific depth toward the bottom up to 121 C at maximum. The salinity variation is parallel to the temperature's; the upper waters from the interface are characterized as low-temperature and -salinity, oxidized, well-mixed, sulfate-rich, chloride-poor acid (pH=2.3) solutions, whereas the lower waters are as high-temperature and -salinity, sulfide and chloride-rich acid (pH=2.7) solutions. XRD and TEM examinations indicated that the bottom sediments consist of kaolinite and smectite associating with a small amount of halloysite in addition to abundant sulfur, pyrite, alunite, quartz, and cristobalite. The altered rocks around the lake contain similar mineral assemblages. Kaolinite of the bottom sediments is characterized as euhedral, large grain-sized, and highly crystalline crystals compared to those from the suspensions in the upper lake water and from the altered rocks around the lake. Halloysite from the altered rocks shows long tubular forms, which differ from short, edge-dissolved, dehydrated tubes in the bottom sediments. Thermodynamic analysis of the lake waters showed that the upper lake water is undersaturated with kaolinite, while the lower water is saturated or supersaturated with it. These data support that kaolinite is in-situ formed and growing up under the Ohyu-numa hydrothermal conditions via dissolving precursor halloysite.

OCCURRENCE OF CLAY MINERALS IN LOS AZUFRES GEOTHERMAL FIELD, MEXICO

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The clay fraction of drill-core samples from the Los Azufres geothermal field (LAGF) have been characterized by X-ray diffraction, in order to study the clay zoning in LAGF, its evolution as a function of depth, temperature and rock composition. LAGF, located in the Sierra de San Andres in the Michoacan State, is the second geothermal resource within the Republic of Mexico. The lithologic successions consist of an andesitic basement overlain by rhyolitic and dacitic domes and flows. Thus, most of the rocks at depth are andesites with a thin cover of rhyolites mostly in the 0-500 m depth range in the central part of the field. The LAGF has given an excellent opportunity to perform a variety of scientific studies through its exploration, development and exploitation stages. Phyllosilicates formed as products of hydrothermal alteration in active geothermal áreas are of great interest since their occurrence is related to the temperature of the environment of formation. In LAGF the clay fraction of cuttings from 20 wells at almost every 100 m was systematically analyzed by X-ray diffraction. To sketch the thermal profile of each well, microthermometric studies of fluid inclusions were done on transparent minerals from the same depth as the clay fraction. Results have been used to locate the distribution of phyllosilicates and isotherms on several cross sections all over the field. Kaolinite, Na and Ca-smectites, mixed layer, illite and chlorite are the common clays and phyllosilicates identified. The relative proportion of each mineral varies as function of temperature, rock composition and depth. Two series of thermal evolution were established for LAGF.

FORMATION OF GRAIN COATING CHLORITE IN SANDSTONES, AN EXPERIMENTAL STUDY

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Grain coating chlorites have long been recognised as an important porosity preserving constituent in medium to deeply buried sandstones. Little is known however, about the precursor material and kinetics necessary for the formation of these coatings. The samples studied were taken from the Veslefrikk field offshore Norway. This field was chosen because the same sandstone formation is buried to different depths due to faulting. Grain coating chlorites exist in the deeper parts of the field (about 3000m burial depth) but not at shallower depths (2500m burial depth). At burial depths around 2500m an X-ray amorphous iron containing coating is present. This coating could act as a precursor to the grain coating chlorite found deeper down in the section. In this study cored sandstone samples with no detectable grain coating chlorite taken from 2500m burial depth and a formation temperature of less than 100 oC were heated to 250-300 oC (at water vapour pressure) in a hydrothermal bomb and later studied electron optically in both scanning and transmission microscopes. Corresponding water chemistry data were also obtained. The experimental results suggest that grain coating chlorite in the natural environment indeed forms from iron rich precursors at burial depths between 2500m and 3000m. The waters from the reaction vessels were also found to be close to equilibrium with chlorite, and add support to this conclusion.

NEW ASPECTS IN THE LOW ANGLE REGION XRD PROFILE ANALYSIS OF SMECTITES

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The search for highly efficient sorbents and catalysts has led to the development of a two dimensional molecular sieve type of materials based on clays. These new clases of materials, known as pillared clays (PILC) are generally prepared by intercalation of smectites with inorganic polymeric cations. The prepared pillared clays require accurate and reliable characterisation. X-ray diffraction characterisation of natural and pillared smectites presented in literature is ususally limited to the apparent d-spacings estimated from the peak maxima in the raw data. It has to be taken into account that the interference function is modulated by instrumental factors (Lorentz-polarization factor, diffraction geometry) and physical factors (structure factor, surface roughness effect). These effects lead to distortions of diffraction profiles, depending on the diffraction angle and peak width FWHM (full width at half maximum). As a result, the diffraction profiles for structures with a large line broadening exhibit a significant peak shift especially at low angles. The neglect of these effects leads to different estimated d-spacings (as presented in the literature) and also can lead to wrong structure models and wrong phase composition determination (two phase sample or mixed structure). Present work deals with the detailed analysis of all these effects, their corrections and their consequences for the interpretation of diffraction patterns. The method will be illustrated on the example of montmorillonites intercalated with hydroxy - Al polymers.

CLAY STRATIGRAPHY OF BRITAIN, ON-SHORE & OFF-SHORE

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The UK Clay Minerals Group is involved with a new synthesis of the clay mineral data available on British sediments, both on-shore and off-shore. Publication is planned for ~2000. This involves an updating and partial replacement of Perrin's original monograph Clay Mineralogy of British Sediments published by the Mineralogical Society in 1971. This monograph has proved to be of great value to all earth scientists, engineers, hydrologists and planners whose professional activities in Britain are affected by clay minerals. New clay mineral data is providing a much more complete view of the regional variations in British sediments as well as novel insights into the role played by volcanism, soil formation and recycling in the origins of their clay mineral assemblages.

INTERCALATION OF NH4+ IN VERMICULITE BY DIFFERENT METHODS

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The interaction between vermiculite and ammonium has been studied by different experimental methods. The Santa Olalla vermiculite was used. It was previously saturated in Na+. The vermiculite was saturated in ammonium by the three following experimental methods: by treatment with NH4Cl solution; by decomposition of n-butylammonium ions previously intercalated. The treatment of the Na-vermiculite with butylammonium solution yields the intercalation of the butylammonium in the interlamellar space, which is degraded into aliphatic chains and ammonium ion. Finally, vermiculite saturated in ammonium is obtained; by reaction with acetamide. A vermiculite saturated in ammonium is also obtained by treatment of this mineral with acetamide involving a hydrolisis reaction.

The samples saturated in ammonium by the three different methods were heated gradually and the loss of water and ammonia was studied. It has been found that both effects are related. The results obtained by IR spectroscopy have allowed to conclude that the type of interaction between ammonium and vermiculite depends on the experimental method of preparation. In the samples obtained by treatment with NH4Cl the results have shown that water molecules take part in the interaction between ammonium and vermiculite. When the ammonium is coming from the decomposition of butylammonium, lower water content is detected in the interlamellar space, due to the hydrophobic character of butylammonium. Practically it does not take part in the interaction between ammonium and the mineral. In the samples saturated in ammonium obtained by reaction of acetamide, it seems that ammonia exists together with ammonium in the interlamellar space.

SMALL MOLECULE EXPLORATION OF CLAY SURFACES

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The concept of active sites has proven to be an extremely useful tool to describe the reactivity of biological macromolecules, enzymes, and proteins. In recent years, this idea has been extended to describe the structure and function of clay mineral surfaces. Analogous to biological macromolecules, the reactivity of clay surfaces can be described on the basis of their active sites. These active sites, or surface functional groups, are defined by the geometric arrangement of surface atoms and by their chemical composition. This framework brings together the concept of surface structure and microtopography with that of reactivity. A useful approach to study these reactive surface features involves the use of in situ molecular probes that can explore surface functionality and sorption mechanisms. In this paper, small molecules including water, ammonia, and hydrazine are exploited as molecular probes to study clay surfaces. Because of their small size and unique chemical properties, these probe molecules can gain access to all regions of the clay surface. In some cases (e.g., hydrazine) these molecules can be used to penetrate into the siloxane surface. Spectroscopic properties of these sorbed molecules are influenced by their close proximity to the clay surface and by site-specific bonding interactions. In this context, they function as molecular probes and can be used to obtain information about the structure and reactivity of the clay surface.

DIVERSE ORIGINS OF VERMICULAR KAOLINITE IN RESIDUAL KAOLIN

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Residual kaolin was formed by weathering of anorthosite in the Sancheong district, Korea. Microchemical and microtextural characterization using scanning electron microscopy and electron microprobe analysis revealed that vermicular kaolinite in residual kaolin was originated from diverse parent minerals and formation *processes as follows. 1) Replacement for primary layer silicates. Vermicular kaolinites were derived from biotite, muscovite, chlorite, and sericite. The kaolinitization was followed by the formation of highly expanded pseudomorphs implying the import of Al and Si. Primary layer silicates as templates for nucleation and growth were important sinks for Al and Si liberated from dissolving plagioclase. 2) Replacement for halloysite aggregates. Halloysite aggregates formed in the early stage of weathering were gradually replaced by vermicular kaolinite with progress of weathering. They have nearly an ideal chemical composition and are commonly coated with thick halloysite aggregates. 3) Growth on the plagioclase surface by direct precipitation from solution. The diverse origins of vermicular kaolinite must be considered in the genetic studies on the weathering profiles of the kaolinite-bearing sedimentary rocks.*

TEXTURE INFLUENCE ON MASS TRANSFERS AND ALTERATION PROCESSES IN CLAY BARRIER

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Hydrothermal experiments on saturated barrier were conducted for 6 months and 4 years in the granite of the STRIPA mine (Sweden). The French clay Fo-Ca 7 (80 % K/S mixed-layer) was compacted (25 MPa) and placed around a steel heater in a 20 cm diameter borehole. The temperature was about 170°C at contact with the heater and only 80°C at clay/granite interface, thus giving a thermal gradient around 10°C/cm. After heating, the initial texture heterogeneity (millimetric aggregates of clays with sedimentary structures embedded in fine clay matrix) was partly (4 years) or perfectly (6 months) preserved. A multi-scale study combining XRD, optical microscopy, SEM/AEM and TEM/AEM, allowed us to clearly evidence mass transfers and alteration processes. EDS analyses and cartography revealed important element migrations under thermal gradient : Al, Si, Fe to the cold parts and the reverse for Ca, Mg to the hot parts. These transfers are sustained by important mineralogical transformations and permanent dissolution/recrystallization process. In the 4 years test, complete recrystallization of clays occurs with transformation of initial K/Ca-Smectite into Mg-Smectite, up to 3 cm from the heater. Percolation process along the thermal gradient has been evidenced and a relationship between redox conditions and percolation fronts is sustained by new crystallization of gypsum and/or pyrite. Mechanisms and swiftness of element transfers, recrystallization, percolation and mineralogical transformations were influenced by texture heterogeneity. They primarily occur in the microscopic clay matrix (6 months and 4 years), in respect to millimetric aggregates, affected only after 4 years.

ANIONIC CLAYS - A CHEAP AND RENEWABLE SOURCE OF BIFUNCTIONAL CATALYSTS

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Anionic clays, so-called Layered Double Hydroxides (LDHs), are, in terms of charge, mirror images of the layer silicate minerals. LDHs include hydrotalcite, pyroaurite and manasseite which occur naturally and can also be synthesised. The clays havethe general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{m-}_{x/m}.nH_2O]$ *where* M^{+2} *and* M^{3+} *are metal cations with ionic radii not too different from that of* Mg^{2+}*. The cations and the hydroxide groups make up the host layers, and anions (*A^{m-}*) and water the guest ones. The systematic arrangement of species in the layers described above results in an LDH structure which is represented by the figure below. The presentation will focus on the multi-faceted approach which has been adopted in seeking to develop some detailed understanding of the intricate phenomena which* underpin the application of anionic clays in catalytic processes. The study has combined the use of neutron scattering methods (quasielastic, inelastic and diffraction) to elucidate the structural and dynamic properties of the clay's hydrogenic species with X-ray diffraction and Fourier Transform Infra-red spectroscopy for establishing the long range order and vibrational modes, respectively. The discussion will include the role played by structural and compositional factors on the dynamics of the water contained in the guest layers, the influence of the host and guest layers on each other and why thermal activation of clays (as is often the practice) need not be a prerequisite to their application as catalysts.

ONE-DIMENSIONAL FOURIER SYNTHESIS IN CLAY ANALYSIS

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The one-dimensional Fourier synthesis from the basal reflections of clays was an important method for the verification of the suggested clay structure by Hofmann (1933). The Fourier synthesis simulates the distribution of electrons and therefor the positions of atoms in the actual layer structure and in the interlayer space of clay minerals. The pioneer works about montmorillonite, vermiculite, mica and chlorite showed excellent results which were mostly calculated by hand. To carry out best results with the Fourier synthesis two basic conditions are required. Firstly a large number of (00l) reflections are needed and secondly the calculated intensities must be compatible with XRD patterns. The large number of basal reflections determine the resolution of the atom positions in the unit cell and can only be achieved with single crystals or carefully prepared high oriented smear slides. In our study, intercalation of propanediol shows more then twelve orders of integral basal reflections for different kind of clays. With a common PC and our new Windows program the calculation of the position of atoms is easily accessible.

A NEW PROCEDURE FOR 40Ar-39Ar DATING OF CLAY FRACTIONS AND GLAUCONITES

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Clay fractions and glauconite lose 30-80% 39Ar during the nuclear transformation 39K(n,p)39Ar in the reactor. As a result, clays could not be dated by the 40Ar-39Ar step heating technique. New observations on 39Ar loss in clay during the irradiation are presented and a new procedure for dating clays by the 40Ar-39Ar step heating technique is proposed. Clays are viewed as composed of two alternating, uniformly distributed basic substrates, the solid material proper and the "non-solid" material, consisting of water and air. The transport behavior of the 39Ar recoils, in the elementary clay particle, was simulated by the Monte-Carlo method. As a specific monitor, an aliquot of the same clay along with its K-Ar age, are used for monitoring the deficit of 39Ar in the irradiated clay fraction. This specific monitor, like any standard monitor, represents the specific conversion of 39K to 39Ar during irradiation and its retention in the solid substrate of the clay. The new procedure is applied without changing the experimental setup. This procedure was successfully demonstrated on the geochronological standard glauconite GL-O and on clay fractions of geologically well studied Turonian sedimentary formations in Israel.

ADSORPTION AND AGGREGATION OF A CATIONIC CYANINE DYE ON SMECTITES

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The adsorption and aggregate formation of a cationic cyanine dye, 1,1'-diethyl-2,2'-cyanine on montmorillonite and saponite have been investigated for aqueous suspensions and cast films. The absorption and luminescence spectra showed the change in the states of the adsorbed cyanine dye. The relatively sharp absorption band at around 570 nm, which is red shifted from the absorption maximum of the PIC monomer, indicates the aggregation of the dye (so-called J-aggregate). In aqueous suspensions, the cyanine dye cations formed J-aggregates on montmorillonite, while they distribute molecularly on saponite. On the other hand, the dye formed J-aggregates on both montmorillonite and saponite in the cast films. Thus, the spectroscopic features of the cyanine dye reflected the difference between montmorillonite and saponite in organizing guest species. The size of silicate particles and the layer charge density of host silicates are thought to be responsible for the difference in the states of the adsorbed PIC. This difference suggests that the cyanine dye can be organized in a controlled manner by the selection of host materials. The J-aggregates formed on the layered silicates may be useful for the study of optical properties of the aggregates because of their stable and confined microstructure.

FORMATION OF AMORPHOUS Al-HYDROXIDE UNDER NATURAL AND ARTIFICIAL WEATHERING CONDITIONS

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Weathering products of K-feldspar collected from the Yakushima granite were investigated by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX). XRD showed that the weathering products formed on the K-feldspar surface were composed mainly of amorphous material with small amounts of halloysite and gibbsite. TEM, SEM, and EDX confirmed that the amorphous material consisted of Al-hydroxides exhibiting a spherical habit less than 1.0 μm and curled fibrous or circular forms less than 0.02 μm in diameter. X-ray photoelectron spectra showed no significant difference in the compositions of weathered and newly exposed unweathered surfaces, suggesting that congruent dissolution occurred throughout weathering. This result also suggested that the Al-hydroxides were precipitated from a leachant solution rich in Si rather than Al. To elucidate formation processes of the Al-hydroxides, low temperature synthesis of Al-Si materials was carried out by the urea method at 100°C for 1 day using acid solutions containing various ratios of Al and Si. Some Al-hydroxides exhibiting similar habits to the weathering products of K-feldspar were formed in solutions having no Si, however the products were strongly affected by the type of anions present. Fibrous Al-hydroxide was produced in solutions containing Cl- and NO3-, but the formation of spherical Al-hydroxide was stimulated in a solution containing SO42-. In solutions having Si/Al > 0.5, allophane or amorphous Si was formed instead of Al-hydroxide.

INDUCED CIRCULAR DICHROISM OF A METAL COMPLEX AS A PROBE FOR THE STUDY OF INTERMOLECULAR INTERACTIONS BETWEEN THE ADSORBED MOLECULES BY A COLLOIDAL CLAY

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The induction of circular dichroism due to a metal complex adsorbed by a colloidal clay was studied in order to investigate the intermolecular interactions between the absorbed species. When an optically active delta-[Ni(phen)3]2+ (phen = 1.10-phenanthroline) was added to an optically inactive [Fe(terpy)2]2+ (terpy = 2.2*.2"-terpyridyl) adsorbed by a colloidally dispersed synthetic saponite, circular dichroism was induced in the electronic spectrum of the latter species. The results indicated that these two metal complexes approached each other on a clay surface in spite of their same positive charge. The dependence of the induced circular *dichroism on time, compositions and temperature was investigated.*

UNIQUE PROPERTIES OF SEPIOLITE AND PALYGORSKITE: IMPLICATIONS FOR USE IN WASTE BARRIER DESIGN

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Prior to the 1980's, poorly regulated disposal of the nation's municipal and industrial wastes created environmental problems, especially with respect to groundwater contamination. Since that time federal regulations have mandated stricter controls on waste disposal. Application of geotechnology to design and construct waste containment systems has become necessary due to such laws. A 1991 survey of waste disposal facilities showed that 61% of the surveyed landfills had liner systems made of clay materials (either recompacted or natural). Ninety-one percent of these facilities specified the use of clay as a cover material in their final closure plans.

Where approved materials are not available on-site, the most economical way to meet containment regulations is through the use of imported clay materials. Clay liners/barriers can provide an effective, inexpensive method to contain wastes. Illite and smectite clay/soil mixtures are the most common liner materials. The clay minerals sepiolite and palygorskite have not been examined for possible use in waste barrier applications. Palygorskite and sepiolite have excellent sorptive properties and, unlike smectites, do not flocculate or channel in the presence of salts. Laboratory studies to asses mineralogy, chemistry, pH, CEC, surface área, Atterberg limits, and hydraulic conductivity of palygorskite, sepiolite, and smectite were performed to determine suitability for waste barrier applications.

Consideration of the unique physicochemical properties of different clay materials can lead to more selective barrier systems appropriate to the waste being contained. Results of these studies are presented and applicability to industrial needs discussed.

PHYSICAL PROPERTIES AND POTENTIAL INDUSTRIAL APPLICATIONS OF A WHITE BENTONITE FROM SAN JUAN PROVINCE, ARGENTINA

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An evaluation was undertaken to determine the development potential of an unusually white Na-bentonite deposit in San Juan Province, Argentina. The units within the deposit range in age from Devonian to Quaternary and consist of a complex series of volcanic events, folds, and faulted shear zones. Breccias, conglomeratic flows, and tuffs are intruded by andesitic, dacitic, and rhyolitic dikes. Smectite and zeolite occur as alteration products within the volcanic sequence. A high degree of variability in clay quality within the deposit and association of the highest grade clay with dikes and shear zones indicate a possible hydrothermal origin for the smectite, as well as surficial alteration by weathering. Samples were collected from the clay layers and evaluated in the laboratory for mineralogy, brightness, swelling, and viscosity. Portions of the deposit show extremely high brightness values for a bentonite; while other áreas exhibit exceptionally high swelling values.

Horizontal and vertical gradations in clay content indicate the possible need for wet processing of the mined material to achieve a quality product. Detailed discussion of the physical properties and potential industrial application of the clay will be shown, along with a proposed process flow sheet.

HEAVY METAL SORPTION ON GLAUCONITE

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Being a clay mineral, glauconite has a relatively high C.E.C. Still, it usually occurs as a granular (sand- or silt-sized) facies in many highly permeable host sediments.

The combination of these properties makes it a potentially useful filter for contaminated waste waters or landfill leachates. Simple experiments on the sorption of heavy metals were carried out on 6 glauconite samples from Cenozoic greensands from Northern Belgium. They had K2O-contents of 7.5, 7.0, 6.9, 6.3, 6.3, and 6.0 %, and total C.E.C. values of 28, 33, 36, 46, 47, and 48 meq/100g. Three series of experiments were carried out. First, glauconite was left to remove metal ions from monocomponant solutions of Pb, Cu, Cd, Ni, Zn, and Cr (added as K2Cr2O7). Depending on the original metal concentration (2.5, 5, 10, 20, and 40 ppm) and on the initial pH (3.5, 5, and 6.5), the following fractions (in %) were removed from the solution: Pb: 98.6 - 100, Cu: 79.8 - 100, Cd: 83.5 - 99.1, Ni: 69,7 - 99.2, Zn: 65.9 - 96.5,and Cr: 10.2 - 100. Experiments with multicomponent solutions (1/3 Pb + 1/3 Cu + 1/3 Cd) and (1/3 Ni + 1/3 Zn + 1/3 Cr) demonstated the following affinity series: Pb >> Cu > Ni > Zn > Cd >>Cr. The release of adsorbed metal ions was studied under different pH conditions (4.5, 6, and 7). Only small fractions of the metal ions were found to be released; maximum fractions were: 0.48 % for Pb, 0.75 % for Cu, 2.55 % for Cd, 1.2 % for Ni,1.7 % for Zn, and 0% for Cr.

THE ASSESSMENT OF MINERALOGIC COMPOSITION OF ROCKS USING FOR LAND RECULTIVATION IN THE SOUTH OF UKRAINE

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Rocks of different geological age were brought to the earth surface from the mining of Kerch iron ore deposit. The physical and chemical properties of some rock substrates presented by loessial loam, clays and sand-clay depositions were studied. The X-Ray analyses on oriented preparations of clay minerals in natural condition, after processing with ethylene glycol and firing were fulfilled using a HZG-4 instrument. It was established that in connection from kaolinite, hydrous mica, montmorillonite content (%) rock substrates can be arranged in three following lines in decreasing order: 1) kaolinite row - green-gray clay (17.8%), loessial loam (4.7), sand-clay deposition (2.6), iron ore including rock (1.8), iron ore slurry (0.7); 2) hydrous mica row - green-gray clay (14.1), loessial loam (7.1), iron ore including rock (1.8), iron ore slurry (0.7); 3) montmorillonite row - iron ore including rock (39.2), green-gray clay (28.1), loessial loam (10.7), iron ore slurry (9.8), sand-clay deposition (7.4).

AN ORDERED MICA/VERMICULITE INTERSTRATIFIED MINERAL

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Soils formed on the Bokkeveld shales of the Cape Supergroup were analysed for soil mapping purposes. During the routine mineralogical analyses of these soils an ordered mica/vermiculite interstratified mineral was found. The Bokkeveld shales are about 395 million years old and were deposited in the Paleozoic erathem. On average the shales consist of 60% biotite and 40% chlorite. This mineral was found in a number of Dystric Regosols. Separate aliquots of the clay fractions of the different horizons were mounted on small ceramic tiles and air dried, glycerol and ethylene glycol solvated samples were prepared of the Mg saturated clay. The K saturated samples were air dried, baked at 100C and 550C respectively. X-ray patterns of all the treatments were obtained on a Philips PW1729 diffraction system.

The clay mineral composition of the soil consists of kaolinite, hydroxy interlayered vermiculite, a vermiculite/mica interstratified mineral and mica. The 24.4, 12.2 and 4.9 peaks were identified as the 001, 002 and 005 reflections of a mica/vermiculite interstratification. The mica/vermiculite interstratified mineral is an ordered structure consisting of approximately 72% vermiculite and 28% mica. The peak shift of the 4.9 reflection of mica to 5.07 is also an indication of the ratio between vermiculite and mica in the interstratification. Hydroxy interlayered vermiculite is a pedogenetic weathering product of mica and/or chlorite in acid soils with mica/vermiculite as an intermediate weathering product. Chlorite is very unstable in acid conditions and forms smectite which in turn changes to non-crystalline material in prevailing acid conditions.

SURFACE MICROTOPOGRAPHIES OF SERICITE CRYSTALS FROM DIFFERENT MODE OF OCCURRENCES

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The gold decoration technique of electron microscopy was applied to as-grown (001) surfaces of sericite crystals collected from many localities in Japan, such as hydrothermal clay deposits, alteration zones of ore deposits, clay veins and fault in the rocks and geothermal alteration zones. The specimens investigated exclusively exhibited growth spirals of either polygonal or circular forms with varying step separations. The morphological characteristics were critically analyzed in relation to their mode of occurrence (massive as hard rock, soft rock, fissure and cavity filling and replacement product in vein-form). It is demonstrated in general that the crystals from the massive altered rock by metasomatism and replacement product in vein-form are characterized by circular growth spirals with narrower step separations, whereas those from the soft altered rock as metasomatism, fissure and cavity filling are characterized by polygonal growth spirals with wider step separations. The growth mechanism and the mode of occurrence of sericite are close relationship each other. The differences between the two are explained based on the understanding on spiral morphology.

SODIUM-CADMIUM AND SODIUM-ZINC MONTMORILLONITES: THEIR ION EXCHANGEABILITY AND XRD PROFILES

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Ca,Na-montmorillonite from Ivancice (Czech Republic) was used for the experimental work. The original sample contains less than 5% quartz. A saturated sodium form of montmorillonite (Na-MMT) was prepared from fraction with grain size less than 5μm by shaking with 1 mol/l NaCl solution after a multiple overnight saturation. Ion exchange equilibria were determined at 20oC using 0.25g of saturated Na-MMT and series of ZnCl2 or CdCl2 salt solutions with various molar concentration of Zn and Cd. The sorption isotherms for zinc and cadmium montmorillonites exhibit a rather similar shape, which depends on pH; the maxima for Cd and Zn sorbed on MMT are very close to each other (e.g., 0.419 μmol/1g and 0.440 μmol/1g, respectively, for pH = 5). It is characteristic for both elements that high level of sorption is reached at low concentration in solution. Leachability of Zn and Cd in deionized water from fully saturated MMT is very similar, but different results were observed for Na. Total amount of Na leached from MMT (after four consecutive leaching runs) is 21.7%. However, only 2.1% and 1.6% were found for Cd and Zn, respectively. A different quantity of Cd and Zn exchanged in Na-MMT influences significantly the shape of the 001 XRD diffraction profile. Profiles *of montmorillonite fully saturated with Na, Zn, and Cd exhibit single maxima at approximately 12.68Å, 14.89Å, and 14.91Å, respectively. Profiles of montmorillonites not fully saturated with one element have profiles with more maxima. The 'd' value for such complex profile corresponding to 1/2 FWHM varies with the percentage of exchanged Zn and Cd and the relationships seem to be of different nature for different elements.*

IN-SITU MÖSSBAUER MINERALOGY OF PLANETARY SURFACES

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One of the key elements in the evolution of the solar system is iron. Its chemistry is strongly coupled to the chemistry of abundant elements as hydrogen, oxygen and carbon. The identification and the relative abundance of iron-bearing phases, and the determination of the ferric (Fe3+) to ferrous (Fe2+) ratio, by in-situ Mössbauer spectroscopy (Mössbauer mineralogy) will provide information about the types of materials present on planetary surfaces and the nature and extent of atmosphere-surface chemical and physical weathering processes. Miniaturized Mössbauer backscattering spectrometers have been developed primarily for the exploration of the planet Mars and the Moon, but are also of interest for space missions to Venus, comets and asteroids. The critical instrument parameters are < 500 g mass, volume similar to a soft drink can, about 1 W power consumption, and about 300 mCi Co57 radiation source. No sample preparation is needed because the instruments operate in backscattering mode. Data obtained for the same sample (powder) in backscatter and in standard transmission mode give equivalent mineralogical information independent of measurement geometry. Besides extraterrestrial applications this new generation of small and portable Mössbauer spectrometers also opens up a whole new field of terrestrial applications in research labs as well as in industry.

MAXIMUM SWELLING VS. MINERALOGICAL COMPOSITIONS: ARE CLAY-SULFATE ROCKS MECHANICALLY STABLE?

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Clay-sulfate rocks are often encountered where tunnels, waste repositories, oil wells and other engineering structures are placed. Swelling of both clay and sulfate minerals raises a severe question: are clay-sulfate rocks mechanically stable? Long term swelling tests were performed on both natural and synthetic clay-sulfate rocks. Mineralogical investigation was done before and after the tests. Besides the conventional conclusions, new understandings may be suggested by present study:
1) A maximum swelling stress (ss) of 6.0 MPa was reached by a natural sample with its foliation perpendicular to the load axis after 2400 days of swelling test. Similar test was done on another natural sample with slightly different mineralogical composition. A surprisingly high ss of 4.8 MPa was obtained where the axial load was parallel to the sample's foliation; 2) Swelling tests on a series of synthetic clay-anhydrite rocks showed that maximum ss of 7.85 MPa can be reached in a sample with 30% of clay and 70% of anhydrite; 3) A maximum ss of 1.05 MPa were obtained from a natural sample which contains 80% of anhydrite and 0% of clay. Other accessory minerals (such as iron minerals and carbonates) or preferable microstructures rather than clay may aid the sole swelling of anhydrite; 4) Small amount of clays in the samples definitely enhance the swelling of anhydrite: 1.05 MPa of ss was obtained from a sample contains 80% of anhydrite and no clay whereas 2.49 MPa for a sample with 80% of anhydrite and 5% of clays.

THE PUZZLE OF MAXIMAL SWELLING OF CLAY-SULFATE ROCKS: POSSIBLE SOLUTIONS USING MICROSTRUCTURAL OBSERVATIONS AND MECHANICAL DATA

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Swelling behavior found in clay-sulfate rocks is a common problem in tunneling, waste repository construction, and other engineering structures. Knowledge on estimating the degree of maximum swelling of clay-sulfate rocks may contribute a great deal to the design, maintenance and safety control of the engineering constructions. The magnitude of swelling stress and strain in clay-sulfate rocks is not only dictated by both physical and chemical interactions (e.g., overburden pressure, porosity, permeability, water and sulfate contents), but also by their mineralogical composition and microstructure. Data obtained from long-term swelling stress and strain tests as well as microstructural observations on both natural and synthetic samples are useful in solving the puzzle of maximal swelling of clay-sulfate rocks. On the basis of microscopic observations before and after the tests of samples, several mechanisms causing the swelling of clay-sulfate rocks are proposed.
1) The overgrown of anhydrite relics by random distributed gypsum crystals indicates the fast transition from anhydrite to gypsum during swelling tests. 2) Gypsification front is controlled by clay layers, grain boundaries and cracks. This feature may reflect that water access and permeability are essential for anhydrite swelling and explain the different swelling pressures and free swelling strains reached by samples with similar mineralogical composition. 3) In addition to the swelling potential, clay and marl clasts are often brittlely deformed and subsequently enhanced anhydrite swelling twofold. 4) Different generations of vein filling by gypsum show a crack and seal mechanism which may explain the stepwise increase in swelling stress during the tests.

STRUCTURE AND PROPERTIES OF ANIONIC CLAYS

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Clays with anion exchange properties constitutes a structurally relatively simple group of minerals (hydrotalcite-pyroaurite). Based on the Mg,Fe(III)-containing mineral pyroaurite (Mg 6-x Fex(III)(OH2)(CO3)x72)nH2O) we focus on the spectroscopically derived coordination of Fe(III) in natural and synthethic samples. We demonstrate that small differences in the coordination of Fe(III) excist, and that this effects is different from texture effects which are particularly prominent in natural samples. In particular, the results of Mössbauer spectroscopy at high (RT) and low (5K) temperatures and in applied magnetic fields will be discussed. The reaction of glycerol with pyroaurite is complex and involves redox, swelling and dissolution. We shall present the results of a series of experiments where we have recorded the progressive changes in structure and chemistry of the reaction. Finally we shall discuss the results from an investigation of the potential environmentally important reaction of Green Rust (the Fe(II)Fe(III) analogue of pyroaurite) with nitrate with emphasis on the redox changes in the solid state.

LAYER NUMBERS OF MONTMORILLONITE IN DIFFERENT CONDITIONS DETERMINED BY HRTEM AND XRD

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To resolve the questions of what are the thickness of raw montmorillonite particles and whether the particles become thinner or not when dispersed in water, the number of layers of montmorillonite particles in the raw state and dispersed states in water were determined by HRTEM, in comparison with the results calculated from the XRD peak broadening. A pure bulky monntmorillonite specimen produced from Aterazawa mine, Yamagata, Japan was coarsely crushed and the ultra-thin sections of about 20-30 nm were made by ultramicrotome. The montmorillonite particles dispersed in water in differentncentrations were also cut i concentrations were also cut into ultra-thin sections. These ultra-thin sections were used to image, by HRTEM, the layer lattice, and the layer numbers were counted on the print.

The basal XRD peaks of montmorillonite were measured for the raw specimen and for each dispersion, and the apparent number of layers was calculated using the Scherrer equation. By the HRTEM observation, the number of layers of the raw montmorillonite particles was not more than 50-60. The mean number of layers in the particles dispersed in water was about 7-10, and sometimes as few as 2. The particles dispersed in water seem to become thinner compared to the raw particles. The number of layers, however, seem to be largely unchanged in dispersions of different concentrations. These number of layers were compared with those determined by XRD. A characteristic structure of raw montmorillonite observed in SEM, like the petals of roses, seems to show a basic particle thickness because the petal's thickness coincided with the number of layers in the raw montmorillonite.

CLAY MINERALOGY OF SOME QUATERNARY DEPOSITS IN THE NORTH-WESTERN COASTAL ZONE, EGYPT

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Clay mineralogy was taken as an indicator for environmental interpretation in Rosetta-Maryut área. X-ray diffraction and differential thermal analysis (DTA) revela the abundance of montmorillonite, illite and small amount of kaolinite in the eastern part of the área which indicates deposition under marine and deltaic environments with alkaline chemical affinity. Deposits of the western part of the área are characterized by the abundance of kaolinite with small amounts of illite which reflects a continental and marshy and shallow marine environment of deposition.

PARTIAL STABILIZATION OF Fe(II) IN FERRUGINOUS SMECTITE

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Reduction of Fe in 2:1 dioctahedral smectites profoundly affects many properties of the clay. Manipulation of the oxidation state to modify these properties could be of great benefit, depending on the stability of the reduced state. The purpose of this study was to devise a method to stabilize the reduced state in smectites.

Reoxidation of Na-saturated reduced nontronites is rapid and complete in water. In the presence of K, however, reoxidation is less complete and becomes even less so with multiple redox cycles. Another method for modifying properties of dioctahedral smectites is to heat it in the presence of Li^+*, causing the small* Li^+ *ions to become attracted to the negatively charged octahedra in the structure, which decreases layer charge and irreversibly collapses the layers. Two Fe-rich smectites were chemically reduced, exchanged with* Li^+*, then heated to 260° C for 24 hr to fix the* Li^+*. The reduced state was largely preserved during* Li^+ *exchange. Upon* Li^+ *fixation, sample SWa-1 retained about one-third of its initial Fe(II) content whereas sample NG-1 was completely reoxidized. Changes in infrared spectra indicated that* Li^+ *entered the octahedral sheet of sample SWa-1, probably creating some trioctahedral domains with LiFe(II)Al-OH environments. The results* *suggest that Li-fixation stabilizes neither Fe(II)Fe(II) nor Fe(III)Fe(II) pairs in reduced smectites, but Fe(II)Al(III) pairs can be stabilized. Thus the greater Al content in sample SWa-1 is the stabilizing factor of Fe(II) in reduced nontronites.*

THERMAL TRANSFORMATION OF A KAOLINITE-POLYACRYLAMIDE INTERCALATION COMPOUND

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Thermal transformation of a kaolinite-polyacrylamide (PAAm) intercalation compound was investigated. Acrylamide was intercalated into kaolinite and was subsequently polymerized to form PAAm between the layers of kaolinite by heat treatment at 300oC for 1 h. The kaolinite-PAAm compound was heated in the range from 460oC to 620oC under a nitrogen atmosphere. XRD patterns of kaolinite-PAAm compounds after heat treatment showed a basal spacing of 1.27 nm, indicating that carbonaceous materials remained between the layers of kaolinite in the temperature range investigated. In 29Si NMR spectra for kaolinite, the Q³ peak at -91 ppm shifted to -100 ppm with an increase in temperature. On the other hand for kaolinite-PAAm compounds, the Q3 peak at -91 ppm shifted to -94 ppm after heat treatment at 500oC and the profile of this peak changed scarcely above 500oC. In 27Al NMR spectra for kaolinite, 6-coordinated Al was converted partially into 5- and 4-coordinated Al, which became dominant with an increase in temperature. On the other hand for kaolinite-PAAm compounds, only small part of 6-coordinated Al was converted into 5- and 4-coordinated Al after heat treatment at 500oC and the ratio of distribution changed scarcely above 500oC. These results indicated that carbonaceous materials between the layers of kaolinite influenced the dehydroxylation of kaolinite. For a kaolinite-PAAm compound, dehydroxylation may occur only within a layer and the tetrahedral sheet may be maintained, so that the dehydroxylation was suppressed. On the other hand, in kaolinite, dehydroxylation may occur between adjacent layers as well as within a layer.

EFFECTS OF SALT CONCENTRATION ON SETTLING PATTERN AND SEDIMENT VOLUME OF LOW-SWELLING SMECTITIC MARINE CLAYS

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The settling characteristics of Ariake clay suspensions with different initial water contents were investigated experimentally under various salt concentrations in the pore water. The settling pattern of a clay suspension is usually classified into four types according to the initial water content and the salt concentration in the pore water: dispersed free settling, flocculated free settling, zone settling and consolidation settling types. The initial water contents of the clay suspensions when the settling types shifted from flocculated free settling, zone settling and consolidation settling to dispersed free settling decreased with a decrease in the salt concentration. Though Isahaya Bay clay and Ariake-kantaku clay contain smectite as the principal clay mineral, the settling patterns of the clay suspensions were similar to illite rather than montmorillonite. In addition, the sediment volume of the clays decreased with a decrease in the salt concentration. This tendency was opposite to that of montmorillonite and similar to that of illite. It has already been reported that the liquid limitof Ariake clay decreases with a decrease in salt concentration, and that this tendency is opposite to that of montmorillonite and similar to that of illite because of the low-swelling property of smectite. Thus, *the settling characteristics of Isahaya Bay clay and Ariake-kantaku clay seem attributable to the low-swelling property of smectite.*

SORPTION OF ORGANIC-COMPLEXED TOXIC METALS BY MODIFIED CLAYS : SURFACE HYDROPHOBICITY EFFECTS

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A great number of toxic metals such as heavy metals, actinides, lanthanides are known to form stable complexes with different naturally occurring organic substances (NOS). On the other hand, the surfaces of clay minerals and oxides in soils and sediments also are generally coated with NOS, which play an important role in interaction of metals with clays. Despite a number of recent works on various aspects of interactions of organic pollutants with clays, mechanisms of sorption on a molecular level of organic-complexed metals on clay surfaces in many details remain unclear. The objective of this investigation was to study the sorption interactions of trace metals and radionuclides (Pb, Co, Cu, Eu, etc) on modified clay minerals in the presence of humic substances. Organoclays were prepared by exchanging the metal cations on the surface and between the clay layers with cations of different quaternary ammonium salts. Samples of organoclays representing a range of hydrophobic/hydrophilic properties were used in batch sorption experiments. It is shown that the mechanism of organic-complexed metal sorption to partly hydrophobic surfaces involves both surface complexation and hydrophobic bonding. In some cases at different surface coverage values stable organoclays with high affinities for organic-metal complexes are produced. The information obtained from this study indicates that organoclays could significantly affect the migration processes of organic-complexed trace metals and radionuclides in the environment. These results suggest that organoclays can be used in antifiltrative barriers for retention of radionuclides and heavy metals from ground waters. Our studies are ultimately aimed at developing strategies for dealing with surface and subsurface environments such as thosesurrounding Chernobyl.

INTERLAYER-ANION ORIENTATION IN A MIXED TEREPHTHALATE-CARBONATE HYDROTALCITE-LIKE COMPOUND

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A hydrotalcite-like compound (HTLC) with a mixture of terephthalate [TA, p-C6H4(COO-)2] and CO32- as interlayer anions (60:40 ratio) and a Mg/Al ratio of about 2:1 was precipitated by addition of a Mg,Al-nitrate solution to an alkaline TA-CO32-solution until a pH of 11 was attained. Separate subsamples of this suspension were aged at 74oC under ambient atmosphere and pressure for periods ranging from 1 h to 4 days, washed by centrifugation with deionized water until nitrate-free, and then dried at 100oC overnight. Although subsequent characterization showed no significant changes in the composition of the HTLC, substantial structural reorganization of the interlayer region was observed during the aging process. The nature of these structural changes was investigated using solid-state nuclear-magnetic-resonance (NMR) spectroscopy [13C static and cross-polarization magic-angle-spinning (CP/MAS), and 2H static one- and two-dimensional experiments], powder X-ray diffraction (XRD), and Fourier-transform infrared (FTIR) spectroscopy in an effort to infer the structural and dynamic processes that occur during aging.

STABILIZATION OF EMULSIONS BY BENTONITES AND DOUBLE HYDROXIDES

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Emulsions are colloidal distributions of an oil in water (O/W-emulsions) or of water in an oil (W/O-emulsions). Usually, emulsions are formed by mechanical dispersion of one compound in the other in the presence of emulsifying agents. There are also practical applications where finely divided solid materials act as stabiliziers (Pickering emulsions). Due to their unique properties clay minerals, above all montmorillonites, should be suitable solid stabilizers for emulsions. However, the stabilizing effect of montmorillonite is very poor. To obtain stable emulsions, certain surface active agents must be added. The advantage of the combined stabilization by montmorillonite and neutral surfactants is that (i) the emulsions are very stable and (ii) surfactants can be used which, in general, are poor emulsifying agents. In contrast to clay minerals, layered double hydroxides are excellent stabilizers of O/W-emulsions, even in the absence of surfactants. Nevertheless, the emulsifying properties are enhanced by a combination of clay minerals and double hydroxides. Creaming of these systems produce solid-like upper phases with high volume ratios of oil (up to 80 %!) and small amounts of water.

SPECTRAL ANALYSIS IN MÖSSBAUER SPECTROSCOPY

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We review some of the recent methods of data treatment and spectral analysis that have been developed for Mössbauer spectroscopy. In particular, the methods that are presented in the satellite Mössbauer Workshop to ICC'97 and that are part of the MOSMOD software package (e-mail: mosmod@physics.uottawa.ca) are described (Rancourt, 1996). The newest of these include a Bayesian inference method (Dou et al., 1995) and an extended Voigt-based fitting (xVBF) method for N-dimensional correlated hyperfine parameter distributions (Lagarec and Rancourt, 1997). The latter xVBF method is particularly well suited to several clay, soil, and sediment related minerals having several hyperfine parameters that are distributed and correlated. Unlike previous models that mostly assume linear couplings between one primary distributed parameter and various slave hyperfine parameters, xFBF allows individual arbitrary-shape partially integrated distributions of all the hyperfine parameters, with any degree of correlation between them. We illustrate the method with various examples related to clay and soil minerals and more complicated multi-phase systems.

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ACCURACY OF FERRIC/FERROUS DETERMINATIONS IN PHYLLOSILICATES: A COMPARISON OF MÖSSBAUER AND WET-CHEMICAL METHODS

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We address the classic problem of accuracy and precision of Mössbauer spectroscopy and wet-chemical ferric/ferrous determinations in phyllosilicates. A suite of

14 well-characterized biotite specimens with various total Fe and ferric/ferrous values and the geochemical standards mica-Fe and mica-Mg were analyzed by 57Fe Mössbauer spectroscopy using the latest experimental and spectral analysis methods developed in our laboratory (Rancourt et al., 1994). These methods include: non-polarizing/non-textured absorber preparation, exact analytic thickness corrections, and quadrupole splitting distribution spectral analysis using our Voigt-based fitting algorithms. The same specimens were also analyzed by two similar metavanadate titration methods from two laboratories and by a potentiometric method from a third laboratory. Mössbauer spectroscopy gives a precision for Fe3+/Fe that is typically 0.001 whereas the best wet-chemical determinations have a precision of 0.02. With regards to accuracy, there is a significant systematic difference between the Mössbauer

and wet-chemistry results: The Mössbauer Fe3+/Fe values are typically 25% larger. To the extent that systematic errors in the wet-chemical method can only lead to overestimates of ferric iron, this proves that, in micas, the Mössbauer recoilless fraction for octahedral ferric iron must be at least approximately 30% larger than the recoilless fraction for ferrous iron. In addition, we note that in the mica-Fe standard, which is available in both powder and granulate form, the powder is significantly oxidized relative to the coarsest granulate fraction, by a factor of three.

Rancourt D.G. et al. (1994): Phys. Chem. Min. 21, 244-249; 250-257; 258-267.

ACTUAL SUB- AND SUPER-STRUCTURE OF FOUR-LAYER CA-BIRNESSITE

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Synthetic Ca-birnessite was studied by X-ray and selected área electron diffraction. Globally, the structure of Ca-birnessite is described with a four-layer monoclinic subcell with a=5.150Å, b=2.844Å, c=4c'=28.16Å, and b=90.3°. Actually, two different varieties of Ca-birnessite may be distinguished from their stacking sequences and super-periodicities. Ca-birnessite type I exhibits a A=3a=15.45Å, B=3b=8.472Å super-cell. Its stacking sequence corresponds to defect-free OSOS stack, where O and S correspond to layer stacks in which successive layers are shifted along a and b axes by ccosb=-0.007a and 0 (O stack), and ccosb=-0.007a and b/2 (S stack). Ca-birnessite type II has a A=12a=61.80Å, B=4b=11.392Å super-cell. Its stacking sequence corresponds to a random interstratification of OSOS (90%) and OOOS (10%) structural fragments. Usually, Ca-birnessite crystals consist of intergrown sub-crystals of both varieties (type III) and have an intermediate b=2.844Å parameter. As in Na-birnessite, the A=3a super-structure arises from the ordered distribution of MnIII-rich rows parallel to [010]. In MnIII-rich rows, heterovalent Mn cations form regular MnIIIMnIIIMnIV (type I) and MnIIIMnIIIMnIVMnIV (type II) sequences. Additional super-periodicities are automatically induced by these regular distributions, and those of associated interlayer Ca. In both cases interlayer Ca provides a local charge compensation being coordinated by pairs of the most undersaturated oxygen atoms, one from each layer. Idealized structural formulae for Ca-birnessite type I and II are Ca2(MnIV14,MnIII4)O36 and Ca(MnIV10,MnIII2)O24, respectively. Because of structural constraints the amount of interlayer Ca is low in both varieties in comparison with exchanged Na-birnessite. Layer vacancies and associated interlayer Na may be responsible for this limited cation exchange.

FIXATION OF Zn BY VERMICULITE AND FE-OXIDE IN WEATHERED GLACIAL SEDIMENTS

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Glacial sediments in a dispersal train derived from a small, marble-hosted sphalerite deposit in eastern Ontario were sampled. Trenching was carried out and samples were collected from vertical sections in order to examine the distribution of Zn in chemical weathering profiles developed on till and related glacial sediments. The sediments have been weathered to bedrock (about 1 m depth). Sphalerite has been completely oxidized; however, the sediments retain high concentrations of Zn (up to 716 ppm). Energy-dispersive spectroscopy and X-ray diffraction indicate that Zn released from primary sphalerite during chemical weathering has been *incorporated into secondary Fe oxides and vermiculite pseudomorphs after biotite (other local lithologies include granite and diorite). A negative correlation exists between Zn and K_2O in biotite, vermiculite, and intermediate phases, indicating that Zn^{2+} was taken up progressively (possibly as a hydrated ion) as K^+ was leached during biotite weathering. Two trends with different negative slopes were defined. Similar trends have been observed by others during vermiculitization in the presence of $CuSO_4$ solutions, where Cu^{2+} was fixed and subsequently reduced to metallic Cu. The presence of Zn in spherulitic Fe oxide indicates that, in addition to ion exchange in clays, coprecipitation was an important process for fixing Zn. The uptake of Zn by vermiculite and Fe oxide may explain why Zn concentrations in stream sediments in the region were below threshold values observed in similar geological settings.*

RARE EARTH ELEMENT DISTRIBUTION IN SOILS DEVELOPED FROM SEDIMENTARY ROCKS

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The distribution of the selected rare earth elements (REEs) in soil pedons developed from Conasauga, Chickamauga, and Knox groups located in the western portion of the Valley and Ridge physiographic province in eastern Tennessee was studied. The selected REEs--La, Ce, Eu, Tb, Yb, and Lu--were quantified by neutron activation analysis. Chondrite-normalized REE plots of the soils showed a higher enrichment of the light REEs and a lower enrichment of heavy REEs, commonly observed in shale and loess samples. The distribution of the total REEs indicates (1) illite-rich clays from the Conasauga shale have a higher total REEs than kaolinite-rich clays from Chickamauga limestone and Knox dolomite, (2) clay fractions have a higher total REEs than either silt or sand fractions, (3) the total REEs increase generally with the depth of the soils developed from residuum, and (4) the total REEs of the soils developed from shales are higher than those of the soils developed from limestone and dolostone. The total REE distribution of the water-dispersible clays from different geologic groups has potential applications in reservoir studies that involve modeling of surface water mixing and soil erosion.

CHEMICAL COMPOSITIONS OF COEXISTING ILLITES AND CHLORITES IN AL-SATURATED METAPELITES OF VERY LOW- TO LOW-METAMORPHIC GRADES, INTERNAL LIGURIDE UNITS, NORTHERN APENNINES, ITALY

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Chemical compositions of coexisting illites and chlorites in Al-saturated metapelites of very low- to low-metamorphic grades (temperature range: 200 to 350 ° C; pressure range: 3 to 7 kb) have been investigated. The main chemical characters of illites consist in an evident deficiency in interlayer cations, an important celadonitic substitution and a slight deviation of the octahedral sheet from dioctahedral to trioctahedral character. Interlayer cation deficiency appears to be controlled by $K^{XII} + Al^{IV}\ Si^{IV} + {}^{XII}$ *substitution and by the entry of some* $(Mg + Fe)^{VI}$ *in the octahedral layer in excess of a full dioctahedral occupancy. The first substitution represents the main mechanism of control: it appears to be mostly dependent on metamorphic temperatures. The small amounts of* $(Mg + Fe)^{VI}$ *producing deviation from a perfect dioctahedral occupancy only balance about 0.2 vacancies in the interlayer sites: this mechanism appears more dependent on bulk rock chemistry than on metamorphic conditions. Most of the Mg and Fe cations present in the octahedral layer (their sum ranging from 0.508 to 0.639 atoms per* $O_{20}(OH)_4$ *) results from* *the celadonitic substitution, which is essentially related to the metamorphic pressures. The main chemical character of chlorites results to be a significant deficiency of octahedral cations: this feature seems to be mostly controlled by thermal conditions, only subordinately by pressures.*

MODIFICATION OF ILLITE CRYSTAL SIZE DISTRIBUTIONS BY SAMPLE PREPARATION FOR POWDER XRD ANALYSIS

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Mean crystallite sizes of illite have been obtained by direct measurements using TEM on ion-milled samples and clay separates, and by XRD profile analysis of clay separates in a prograde sequence of metapelites from southern New Zealand. The mean crystallite sizes determined by the analyses of peak profiles on clay separates increase with metamorphic grade, consistent with the trend determined by TEM from ion-milled samples. However, the crystallite sizes obtained by TEM on ion-milled samples are approximately 2 to 4 times larger than those by XRD profile analyses. This difference is greater in higher grade than lower grade samples.

The mean crystallite sizes measured using TEM on the clay separates that were used to obtain XRD profiles are similar to those from XRD profile analyses. These relations indicate that the XRD data were obtained from samples that differ significantly from the original rock samples. Furthermore, the data indicate that sample preparation for XRD analysis significantly altered the original crystal size distributions. All separates have log-normal size distributions; such distributions are well-known to be characteristic of cleaved separates as a result of the disaggregation process. Log-normal size distributions of clay separates have been taken as direct evidence for crystal growth mechanisms, but the results of this study demonstrate that such conclusions are generally not warranted. Only crystal size distributions of unseparated samples, or separates where the effects of the separation process are known, should be used as indicators of growth conditions.

WEATHERING PROFILES OF BIOTITE-GNEISS IN RIO DE JANEIRO BRAZIL

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Three weathering profiles (Niemeyer, Jacarepagua and Vista Chinesa profiles) located in 3 different positions of the "Macio da Tijuca present similar lithologies (biotite-gneiss) but different microclimate and relief. Their composition and evolution from the unaltered rock up to the pedologic horizons A, AB and B were defined. Thirty-six samples were studied by x-ray diffraction, optical petrography, SEM/EDS and chemical analysis. The 3 profiles are composed of biotite, quartz, feldspars, garnet, cordierite and traces of sillimanite and muscovite. Despite their similar lithologies, they present a variable evolution. The clay mineralogy of the Niemeyer profile is composed of illite, halloysite, illite-smectite and traces of kaolinite-smectite. The Jacarepagua profile presents kaolinite and 10Å halloysite whereas the Vista Chinesa profiles presents illite-vermiculite, kaolinite, gibbsite and traces of interstratified kaolinite-smectite. The great thickness of the Jacarepagua profile (110m) is probably due to the fact that the rock layers dip in a direction perpendicular to the topography which favors fluid infiltration, rock alteration and prevents mechanical removal of the layers. Differently, the Niemeyer profile is composed of a rhythmic interlayering of pellitic and quartz-rich rocks and sets concordantly with the topography, allowing a great removal of the layers and precluding the evolution of the clay mineral to the 1:1 type. The Vista Chinesa profile presents 2:1 type clay minerals, which are less evolved than the ones in the Jacarepagua profile, probably due to the removal of more evolved clay minerals in the *past. These results show that the slope stability of the Niemeyer profile is more critical than the others.*

SINGLE INTERLAYER TRANSFORMATION OF ILLITE-SMECTITE-VERMICULITE IN NORTH SEA JURASSIC SHALES

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For mixed-layer fractions from shales from oil wells in the North Sea and onshore Denmark, X-ray diffractograms have been recorded for specimens saturated with Mg, Ca, Na, and NH4, both air-dry and intercalated with ethyleneglycol, and the patterns have been computer-simulated with a multicomponent program, the multispecimen fitting technique. Furthermore, the distribution of K and NH4 in the illite layers has been determined by a new XRD method. The mixed-layer fractions consist of an illite-smectite-vermiculite (I-S-V) phase constituting ~90% of the fraction and a kaolinite-illite-vermiculite (K-I-V) phase. I-S-V of predominantly detrital origin has 0.69-0.73 illite, 0.26-0.20 smectite and 0.04-0.07 vermiculite interlayers, the illite, smectite and vermiculite interlayers being segregated. Diagenetically transformed I-S-V has 0.80-0.84 illite, 0.12- 0.08 smectite and 0.08 vermiculite interlayers, the vermiculite interlayers being segregated whereas the illite and smectite have the maximum ordering possible for R= 1. Solid-state 27Al and 29Si NMR show that the illite interlayer formation is accompanied by Al for Si substitution in the tetrahedral sheets. Analyses of occurrence probabilities demonstrate that the dynamics of the I-S-V transformation can be described as a single interlayer transformation (SIT) of smectite to illite interlayers within the crystallites. This transformation mechanism explains the finding that the detrital illite layers are potassium illite whereas the new-formed illite layers are in fact tobelite layers. The K-I-V phase may well be mistaken for kaolinite having small coherent scattering domains. However, application of the multispecimen fitting technique demonstrates that this phase has ~0.94 kaolinite, 0.03 illite and 0.03 vermiculite layers and random ordering. During diagenesis, this structure does not change but the amount of this phase decreases probably due to dissolution.

NOVEL SYNTHESIS OF ALLOPHANES FROM ALL-ORGANIC EDUCTS IN ORGANIC SOLVENTS

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The method of employing all-organic educts in an organic solvent in order to synthesise purely inorganic materials ought to be a new and attractive way leading towards novel materials with unique properties. Allophane - hollow spherical hydrous alumosilicates with diameters of 3.5 to 5 nm - was chosen as the target material due to its particular structure which implies abundant possible applications. The walls of these 'nano balloons' are basically made of two layers, one consisting of octahedrally co-ordinated aluminium and the other of tetrahedrally co-ordinated silicon. Allophanes with diameters ranging from 3 nm to 5 nm have been successfully synthesised using organic precursors like tetraethyl orthosilicate and aluminiumtri isopropylate at concentrations of 1 to 10 mmol/l. The Si/Al ratio was kept constant at 0.5 for all experiments. The reactions were carried out in dry organic solvents (e.g. n-hexane) at room temperature and were completed after one to two days. Water, used as a reactant, was added only very slowly via the gaseous phase. Gradual hydrolysis of the organic precursors and successive *poly-condensation lead to the formation of allophanes. As they are almost X-ray amorphous these were identified and characterised by transmission electron microscopy. Remarkably allophanes seem to be kinetically and energetically favourable under the chosen reaction conditions. As by-products imogolite-like tubular structures (tube diameter ~2.5-3 nm) and sheet-like material were observed.*

CRETACEOUS FLUVIAL STRATA IN THE MOOSE RIVER BASIN OF ONTARIO, CANADA, AS A MAJOR SOURCE OF KAOLIN FOR USE IN FINE PAPER AND CERAMIC PRODUCTION

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Poorly consolidated kaolin bearing fluvial strata of the Cretaceous Mattagami Formation, underlie 7000 km2 of the Moose River Basin of Northern Ontario. Analysis of core and logs from 95 closely spaced holes from a 1.8 x 1.8 km área of claims held by Minerals Research Canada, confirm that the sequence is a product of deposition from low gradient anastomosed rivers in which bank stability was maintained by dense vegetation. Statistical analysis indicates a close correlation of both modal grain size and depositional facies, with chemical and physical properties. Kaolin content is highest in grey (average 60%) and light brown to white mudrocks (56%) of distal flood plain facies. Illite content is higher in grey, black and dark brown mudrocks (ball clays) which accumulated in áreas of the floodplain with more stable seasonal water-levels. Medium to fine sands of levee origin contain about 14% kaolin. Channel sands and gravels, have the lowest concentration of kaolin (9%), produced by in situ diagenetic alteration of feldspars by acidic oxygenated ground water in a tropical to subtropical climatic setting. The high reflectance of kaolin in the channel facies makes it highly suitable as a filler in the production of fine paper. The block examined contains reserves in excess of 30 million tonnes of kaolin and ball clay, by extrapolation the ultimate scientific reserves of the Moose River Basin may be in excess of 6.5 x 1011 tonnes.

SURFACE PROPERTIES OF THE IRON OXIDES FORMED AT VARIOUS CITRATE CONCENTRATIONS

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Surface properties of iron oxides directly affect their behavior in soils and associated environments. The surface properties of the iron oxides formed in the presence of citrate ligands at citrate/Fe(II) molar ratios(MR) of 0, 0.001, 0.01 and 0.1 at pH 6.0 were studied. In the absence of citrate ligands, goethite, maghemite and a small amount of lepidocrocite were formed. In the presence of citrate ligands at the MR 0.001 and 0.01, lepidocrocite was formed. The presence of citrate ligands at the MR of 0.1 resulted in the formation of amorphous Fe oxides. As the MR value increased from 0 to 0.001, the total surface área and mesopore surface área decreased with increasing crystallization of lepidocrocite and no micropore was formed in the precipitates. When the MR increased to 0.01 and 0.1, however, the total surface área increased and the micropore was formed because of the formation of poorly crystalline to amorphous products. The average pore diameter of the samples increased as the MR values increased from 0 to 0.001 and then decreased at the MRs of 0.01 and 0.1. The PZSE decreased with increasing the MR as a result of citrate anion coprecipitation. The variable surface charge of iron oxides was increased by the presence of citrate ligands during their formation, especially at the MR of 0.1.

"AMORPHOUS" DERIVATIVES OF ALUMINOSILICATE CLAYS: NEW MATERIALS WITH MULTIPLE USES

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A new family of materials derived from the modification of common, alumino-silicate clay minerals show properties such as increased cation exchange capacity and surface área compared with the original starting clay. These new materials are generically termed kaolin "amorphous" derivative - or KAD - because initial experiments using kaolin as source clay gave a product with a broad hump between 17 and 35 degrees two theta using powder XRD. Recent work has shown that the source clay is not restricted to kaolin. KAD materials mostly retain the basic composition of kaolins with the addition of an exchangeable metal cation such as potassium or sodium. This potassium or sodium cation can be removed from the KAD material by exchanging with other metal cations in solution. Metal ions with which KADs will exchange include: Li+, Mg+2, Al+3, Ca+2, V+4, Cr+3, Mn+2, Fe+2, Co+2, Ni+2, Cu+2, Zn+2, Ag+, Cd+2, Nd+3, La+3, Hg+2 and UO2+2.
CEC values range from ~100 to 800 meq/100g for 1M solutions depending on the nature of the exchanging ions. Surface área values for KAD materials range from ~25 to 250 m2/g and can be varied by careful manipulation of the process chemistry. A wide range of applications for this new derivative of aluminosilicate clays has been identified in the general área of environmental remediation.

AGRICULTURE AND PHYSICOMECHANICAL PROPERTIES OF COMPACT SOILS

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The investigated black compact soils are located in Alazan Valley in Eastern Georgia. The climate is characterised by alternation of annual wet and dry seasons. The black compact soils studied are noted for high clay content (>40%) and predominance of montmorillonite. They are structureless or weakly aggregated. Aggregates <0,25 mm in diameter predominate. In water they break down into fine clay-size particles. Their high bulk density under dry conditions is closely related to capillary and fine pore formation. Compact soils swell from 24 % up to 40 % in accordance with the initial moisture content. In the course of the swelling at the initial moisture content 12-18 %, swelling pressures as high as 4-7 kg/cm2 are observed. High swelling pressure makes considerable modifications in structural - textural properties of these soils, causing the disruption of plant roots. Disjoining pressure significantly compresses microaggregates, bringing together both particles and microaggregates. In points of contact between particles stronger structural bonds are formed. They resist the disjointing pressure of water during swelling. The resistance to disjointing pressure is 17 kg/cm2 at initial moisture content of 2,4 percent. In dry season compact soils are subjected to shrinkage up to 12-14%, maximum shrinkage taking place at the humidity of 5%. Strong compactness of soils is caused by the absence of structure and coarse particles, which prevent compact particles 'distribution in the soil and formation of contact points between particles. Compact soils have some negative properties due to abovementioned phenomena, what hampers their sustainable use.

HYDROUS NICKEL-CONTAINING CLAY-LIKE MINERALS IN KARSTIC ENVIRONMENT

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Geochemical studies of karst-bauxites clearly indicated a downward enrichment, culminating at the base of the deposit, of Ni, Co, Cu and REE. This was caused by percolating waters in a highly drained karstic environment. Finally, the footwall limestone acted as an effective alkaline barrier and caused the precipitation of these elements and formation of nickel clay-like minerals, REE-minerals, etc. In this way, when original clayey material was rich in nickel, karstic nickel deposits were *formed. Karstic environment is poor in silica, but rich in alumina. Therefore, nickel clay-like minerals are either silica-free, or have relatively low* SiO_2 *content.*

Usually, they are Ni-Al minerals. Nepouite, with Si:/(Ni, Mg) = 2:3, is a major nickel phase in karstic deposits, with formula approaching close to the nickel end member of the lizardite-nepouite series. Brindleyite, a nickel-rich aluminous serpentine, has even less silica, and takovite, a nickel aluminium hydroxy-carbonate, is silica-free. These two minerals were found in some karst-bauxite deposits.Recently, a new nickel-rich clay-like mineral was discovered in the Aghios Ioannis karstic nickel deposit in Greece. It is a green hydrous Ni-Al probably layer silicate, mixed with halloysite in various proportions. The strongest reflections: 11.8 (Int. 80), 5.90 (60) and 3.937 (100); two endothermic peaks on DTA: at 92 C and 450 C; SiO_2 *27.50,* Al_2O_3*25.30, NiO 32.90, LOI 14.30 %. The same mineral was described as admixture of takovite in the original locality Takovo.*

KAOLINITE PARTICLE ELECTROPHORESIS IN MINERAL OIL

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The dependence of kaolinite (CEC 20 mc-ekv/g) particle velocity on electric field intensity and particle size in mineral oil were studied by microscopic method in electrophoretic cells having plane-parallel or needle/plane electrodes. In homogeneous field the particle motion is specific for nonlinear electrophoresis. Ten mcm particles move towards the negative electrode and their velocity increases as the square (and more) of field intensity from 0.7 to 2.0 kV/cm. Particle velocity increases approximately as the squared function for particles with sizes from 10 to 40 mcm due to increasing double layer polarization. The positive charge is due to the absence of exchange cation dissociation under their full compensation of surface charge. The excessive negative charge of oxygen and hydroxyl groups at the crystal surface, determining the exchange capacity and titratable acidity (20mc-ekv/g), is compensated in oil dispersive medium by exhange Ba^{2+} *cations without creation of diffuse layer. Electroosmotic sliding in this case takes place with* Ba^{2+} *ions being the potential-determining ions. According to alternative mechanism, the main type hydroxyl groups (12 mc-ekv/g) in oil dispersive medium are blocked less than acid groups and leads to positive surface charge. Sodium dodecylsulfate or synthanol addition increases particle velocities. Zinc dialkylthyophosphat decreases electrophoretic mobility of kaolinite particles to zero. In nonhomogeneous field, particle motion is independent of electrode polarity change. The particle velocity at fixed distance from electrode is the square function of field intensity and particle size. Velocity decrease is not observed upon adding zinc dialkylthyophosphat providing evidence of domination of the dielectrophoretic mechanism of particle charge formation in the case of nonhomoheneous field.*

A SIMPLE AND INEXPENSIVE METHOD TO QUANTIFY THE CLAY FRACTION IN OXISOLS

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Kaolinite is one of the most commonly occurring clay minerals in soils, particularly those in warm, moist climates. It is the dominant clay mineral in the different Oxisols in Brazil; these soils have intrinsically very low fertility. Because of this low soil fertility, many management problems may occur. These problems have, in some situations, been associated with the components of the clay fraction (e.g., phosphate adsorption). Improvement of the quantification and interpretation of the clay fraction may increase our understanding of the fertility management problems. Most methods used to quantify the clay fraction frequently include expensive equipment and software, which may not be affordable for many researchers. In this preliminary study, we tried to quantify the clay fraction of 14 soil samples from A *and B horizons using an inexpensive method based on Resende et al., (1987) to allocate the clay fraction. Our procedure uses preexisting data commonly available in soil surveys; therefore only one x-ray analysis is necessary, in addition to limited chemical analyses. We compared our procedure to differential thermic analyses (DTA) for kaolinite for 14 samples. In all but one, the difference between our allocation method and DTA was between 1 and 5%; in the remaining it was 10%. These results suggest that the utilization of the standard clay for DTA analysis should be reconsidered. Gibbsite, hematite, and goethite were also determined by allocation from preexisting data. These results are promising and will permit large number of researchers to quantify the clay fraction.*

MINERALOGY OF VOLCANIC SOILS AND PALEOSOLS IN SAO MIGUEL ISLAND, AZORES

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The mineralogy of 8 recent and buried Andosols, developed in a volcanic district in Sao Miguel island, has been investigated in order to detect changes in past and recent pedoclimatic conditions. The study site has been chosen because of its geographical position which ensures minimum climatic variation and low eolian contamination from other geological districts but also because of the presence of many buried soils. Soil descriptions along with routine chemical and some mineralogical analysis (X-ray diffraction (XRD) and differential XRD) have been carried out on two recent soils and six buried soils. Recent soils have a pH of 5.5-6.5 and the clay fraction is always lower than 4%. Their clay fraction is dominated by low order material and the amount of Fe oxides in the bulk samples is low having Fed (Fe solubilized with citrate-bicarbonate-dithionite) content of 3-21 g kg-1, the Feo/Fed ratio ranged is 0.5-0.9. The buried soils have a pH of 6.8-7.1 and a clay content of 4.21%. The clay fraction is mainly characterised by halloysite minerals having a strong reflection at 1.0 nm; a moderate content of Fe oxides can be inferred by the Fed values of 17-60 g kg-1; the Feo/Fed ratio is 0.2-0.4 which indicates a good degree of crystallinity. In all six buried soils the main Fe oxide mineral is goethite. Such chemical and mineralogical differences depict a recent allophanic environmental, moist in the whole year, where vitric and typic Andosols develop while the past environmental conditions, as inferred from the buried soils, show a more seasonal pedoclimate where Fe oxides and halloysite can well develop.

STRUCTURAL MECHANISM OF CoII OXIDATION BY THE PHYLLOMANGANATE Na-BUSERITE

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The geochemical association of cobalt and manganese at the Earth's surface results from the oxidation of highly soluble CoII to weakly soluble CoIII, coupled with the reduction of MnIV/MnIII to MnII. The structural mechanism of this redox reaction was investigated at the Na-buserite surface by X-ray diffraction, and powder and polarized EXAFS spectroscopy. The proportion of interlayer cations and layer vacancy sites, CoII/(CoII+CoIII) ratio, the nature of Co sorption sites, and the proportion of interlayer vs. layer Co, were determined for different Co/Mn ratio. From this in-depths structural characterization two distinct oxidation mechanisms were identified. The first mechanism is associated to the fast disproportionation of MnIIIlayer according to 2MnIIIlayer --> MnIVlayer + #layer + MnIIsolution, where

# denotes a vacant site. CoII sorbs above/below a vacant site (#1), and is then oxidized by the nearest MnIIIlayer. The resulting Co species fills in the #1 position while the reduced manganese migrate to the interlayer or in solution creating a new vacant site (#2). This reaction can be written: CoIIsolution + #1 + MnIIIlayer. --> CoIIinterlayer + #1 + MnIIIlayer --> CoIIIinterlayer + #1 + MnIIlayer --> CoIIIlayer + #2 + MnIIsol/interlayer. The second mechanism involves the replacement of MnIIIinterlayer by CoIIIinterlayer, and is eventually followed by the lattice migration of CoIIIinterlayer, depending on the chemical composition of nearby layer octahedra (avoidance of MnIIIlayer - CoIIIlayer - MnIIIlayer sequences). This second mechanism can be schematically written: CoIIsolution + MnIIIinterlayer + # --> CoIIIinterlayer + # + MnIIsolution --> CoIIIlayer + MnIIsolution, the last step being conditional. The confrontation of these structural data to those obtained for natural Co-containing phyllomanganates indicates that the two structural mechanisms observed in the laboratory satisfactorily accounts for observations made on natural samples.

MÖSSBAUER STUDY OF CHLORITE AND TALC FROM THE TRIMOUNS DEPOSIT (PYRENEES, FRANCE): EVIDENCE FOR SYSTEMATIC PRESENCE OF [4] Fe3+

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Six ores from the Trimouns talc and chlorite deposit (Pyrenees, France) are studied by Mssbauer spectroscopy. These ores result from the metasomatic alteration of different rocks, talc-ores (two samples) from dolostones, and chlorite-ores (four samples) from silico-aluminous rocks (mica schists and pegmatites). The bulk Fe2O3 content is under 1 % for talc-ores and between 2.5 and 5 % for chlorite-ores and the iron is located in the talc and chlorite lattice. We have applied the Mssbauer Spectrometry (at 300°K and 4°K) to determine the iron distribution among the different sites of chlorite and talc. We show the systematic presence of unusual [4]Fe3+ in both types of minerals and note for the [6]Fe2+ a different distribution in the chlorite sites depending on the origin (mica schists or pegmatites) of the ore.

APPLICATION OF BASIC CLAYS IN MICROWAVE ACTIVATED KNOEVENAGEL CONDENSATION: PREPARATION OF, -UNSATURATED ESTERS

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Basic solid and base catalyzed reactions are receiving a great deal of attention in the last years, due to the fact that this is an unexplored field which offers possibilities for selectively catalyzing reactions involved in the production of fine chemicals and commodities. Besides the classical low surface área alkaline earth solids, and strong metal alkaline catalysts, researchers have looked to the milder high surface área basic compounds, which can combine base catalysis and, in some cases, shape selectivity. Among the high surface base solid catalysts, alkaline sepiolites present high basicity. In this work, we have studied the catalytic activity and selectivity of a series of alkaline sepiolites for the Knoevenagel condensation of benzaldehyde with activated methylenic compounds. Considering all the experimental procedures induced by heterogeneous media, microwave irradiation exhibits, under milder conditions, an interesting reactivity and it has been recently employed to activate some organic reactions catalyzed by inorganic solids. In view of this, this work has studied the effect of the microwave irradiation on the reaction rate, and we report the effect of the operating conditions (Irradiation time, irradiation power and catalysts). A sepiolite supplied by Tolsa (Madrid, Spain) was used as raw material. Na+ and K+ exchanged samples were prepared by treatment with solutions of the corresponding chlorides. The reaction mixtures were irradiated in Teflon closed flask at different powers. The reaction was followed by GC-MS. Under our experimental conditions, we have found that, -unsaturated esters are selectively obtained in a good yield.

GENESIS OF KAOLIN MINERALS IN SEAFLOOR HYDROTHERMAL SYSTEMS

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Hydrothermal clay mineral assemblages of seafoor mineralization are well preserved in the middle Miocene Kuroko-type volcanogenic sulfide deposits in Japan. Mica, chlorite, smectite, and their mixed-layer minerals are dominant hydrothermal alteration products in these deposits. Kaolins (kaolinite and halloysite) were found only in the deposits where the filling temperatures of fluid inclusions in quartz and sphalerite are <200oC, whereas mica and chlorite occur as the predominant alteration product in the deposits where their filling temperatures are >250oC. Barite and native sulfur are associated with these kaolins. Kaolins are also observed in the active seafloor hydrothermal system (JADE) in the central Okinawa Trough. Altered epiclastic sediments and pumiceous tuffs around active hydrothermal vents contain kaolins (kaolinite and halloysite) as well as mica, Mg-rich chlorite, talc, montmorillonite, and mixed-layer minerals of dioctahedral chlorite and montmorillonite. Crusts of native sulfur and barite occur as the marginal parts of the vent áreas. Kaolin minerals have also been found in hydrothermal plumes along the spreading center on the southern East Pacific Rise from 17o30'S to 18o40'S. These plumes contain native sulfur and they have high S/Fe (>1) molar ratios, indicating that the H2S/metal ratios of their hydrothermal fluids are very high. The acidic hydrothermal fluids (T=200 to 340oC and pH=3.1 to 3.4) which formed the plumes were discovered from áreas of active venting on segments around 18o15'S and 18o26'S. These low pH hydrothermal fluids suggest that the kaolins in the plumes were formed by hydrogen metasomatism.

BIOLOGICAL RECULTIVATION OF THE RED-BROWN CLAYS

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Pliocene and post-Pliocene deposits may be used as material for creation of agricultural lands in the steppe zone of the Ukraine with biological recultivation of lands which were disturbed by the mining industry. Red-brown deposits are accumulated to a depth of 7-12 metres and they are characterized by hard ecological conditions for agricultural plants. These problems are nutrient deficiency (in the first N and P) and high content of readily soluble salts (to 3.4%). In spite of this, the top part of the deposits, which are removed on the day surface, is subjected to desalination. Despite this, the red-brown clays and loams contain forms of gypsum and calcium carbonate. In connection with this the possibility of solonetzization is practically excepted. The nutritional deficiency is removed thanks to use of organo-mineral fertilizers and by means of phytomelioration (sowing of perennial leguminous plants). In the long-term field studies, the possibility of using red-brown rocks as substrate for creation of agricultural lands has been determined. A crop rotation with the portion of bean cultures at 80% was proposed for melioration of red-brown rocks.

SYNTHESIS AND MINERALOGICAL PROPERTIES OF A REGULARLY INTERSTRATIFIED 2:1 MARGARITE AND BEIDELLITE (34Å PHASE)

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A regularly interstratified 2:1 composition of margarite and beidellite was hydrothermally synthesized at 400-500C under 1 kbar pressure. The starting material was a mixtures of kaolinite, calcium oxide or carbonate, and alumina gel. X-ray diffraction data of the sample saturated with Mg showed that the spacings of basal reflections varied with different treatments, as illustrated by the first-order reflections observed at 34.6, 29.1, 36.4 and 37.0 under air-dry condition with 60% relative humidity, after heated at 600C and treated with ethylene glycol, and after solvation with glycerol, respectively. The spacing of the 060 reflection was 1.478 indicating the dioctahedral nature of the mineral. Chemical data gave a structural formula of Mg0.18(Ca1.84Na0.22K0.12) (Al5.97Fe3+0.01Mg0.03Ti0.06)(Si7.35Al4.65)O30(OH)6. Differential thermal analysis showed a few endothermic peaks below 200C and in the 500-650C range, and an exothermic peak at 1070C. XRD and chemical data indicated that the mineral is composed of margarite- and beidellite-like layers with a ratio of 2:1. Infrared absorption spectra of the mineral showed major bands at 670-700cm-1 and 900-930cm-1 regions which were reminiscent of those of margarite. This and chemical data suggested that the mineral has a large substitution by Al for Si in tetrahedral sheets.

PILLARED CLAYS AND THEIR APPLICABILITY TO REMEDIAL CONSTRUCTION

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The sealing of waste deposits is a present day problem for the protection of the environment. Nowadays the use of clays as bottom liners is common because of their low hydraulic conductivity for leachate and the high adsorption capacity for cations and anions. However, an important problem is the shrinking of the clay layers due to either interactions with concentrated organic pollutants in the leachate (e.g. saturated, unsaturated and aromatic hydrocarbons, alcohols, phenols, aldehydes etc.) or elevated temperatures (normally in the range of 60-80°C) caused by biochemical decomposition reactions. This work focuses on inorganically pillared clays (PILC) and their uncalcined precursors with respect to their use in bottom liners in the future. Al-, SiAl-, Zr- and Cr-polyoxocations were intercalated into different clays (Cheto and Wyoming type montmorillonites and vermiculite). The uncalcined and calcined products were investigated with respect to their temperature and long time stability as well as their adsorption capacity for chlorophenols and heavy metals. It was not possible to intercalate the large polyoxocations into vermiculite due to its high charge density. Furthermore, pillared Cheto and Wyoming type montmorillonites showed different temperature stability. Cr-pillared clays had a very low temperature stability, even when heated in an Ar-stream. Proceeding from the temperature and long time stability investigations, Al-, SiAl- and Zr-PILC seem to be appropriate for the use as bottom liners.

THE CRYSTAL STRUCTURE OF AN UNNAMED Na-Ca FLUOROSILICATE HYDRATE FROM MONT SAINT-HILAIRE, QUÉBEC

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A new Na-Ca fluorosililicate hydrate has been found in marble xenoliths at the Poudrette quarry, Mont Saint-Hilaire, Québec in association with microcline, narsarsukite and a clinoamphibole. Its structure has been solved by direct methods using single-crystal X-ray diffraction and refined to=20R =3D 4.7 % and wR2 =3D 15.7 %. Results from the structural analysis confirm the mineral is triclinic,indicate P-1 to be the most probable space group and yield the ideal chemical formula

(Ca,Na)3(Na,Ca)6Si10O38(F,OH)2.3H2O. The mineral is a layered silicate, with individual layers composed of six-membered silicate rings cross-linked by shared SiO4tetrahedra along a and c. Two such layers are directly joined along b(the stacking direction) to form a diphyllosilicate unit, with weakly held H2O molecules positioned in the centre of the two layers. The TT units are linked along b by an octahedral layer composed of CaO6 and NaO5F polyhedra, thus forming a TT-O-TT composite unit. Relatively weak bonding between the TT units and the O layers results in a pronounced {001} cleavage,with the strongly bonded TT unit imparting a noticeable brittle fracture to the mineral. The mineral is chemically and structurally related to reyerite, (Na,K)2Ca14Si22Al2O58(OH)8.6H2O (P-3), which is found in hyperalkaline rocks at Niakornak, Greenland, similar to those encountered at Mont Saint-Hilaire. Differences between this new mineral and reyerite result from variations in the geochemistry of the environments of formation and unique stacking sequences of the TT units.

THE CRYSTAL CHEMICAL CHARACTERISTICS OF PALYGORSKITE FROM ANHUI PROVINCE, CHINA

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Significant deposits of palygorskite are present in SE China. These are of two genetically distinct types, a sedimentary variety, developed by pedogenic alteration of a montmorillonite Vertisol, and a hydrothermal palygorskite, produced by hydrothermal alteration of a siliceous dolomitic marble. Palygorskite has an ideal formula (Mg,Al,Fe3+)5[Si8O20](OH)2(OH2)4.4H2O. WDS and XRF analyses indicate octahedral cation sums of 3.70 to 4.4 per formula unit. As this is slightly below the ideal value of 5, vacancies must exist at this site. In addition a significant presence of interlayer cations is indicated, with sums ranging from 0.04-0.40 cations p.f.u. for both types of palygorskite. Palygorskite of hydrothermal origin is rare; it occurs in compact, coherent masses of 'mountain leather' in which crystals are typically 2-5 µm long and are white and fibrous. Palygorskite of sedimentary origin in the Pliocene Xiacowan Formation consists of thick clay beds containing grey to white, clay-sized fibres, with lengths of 0.5-5 µm. The hydrothermal palygorskite has a characteristically higher Al2O3 and lower Fe2O3 content than the sedimentary variety. X-ray diffraction studies indicate that the sedimentary material is predominantly monoclinic in symmetry, whereas the hydrothermal material is orthorhombic. Infrared and differential thermal analysis for both types are very similar. These, along with XRD studies indicate that the hydrothermal material has a higher degree of crystallinity.

THE LOWER LIMIT OF THE CATION EXCHANGE CAPACITY OF A COMPLETELY SWELLABLE CLAY

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Most swellable clays have a cation exchange capacity between 75 to 150 mmol/100g clay. Hectorite is known as a clay with the lowest CEC (75mmol/100g) and the lowest charge density (0.28 per half unit cell). According to the Hofmann Klemen effect, there is no limit for reducing CEC by neutralization of the charge using lithium incorporation into the empty octahedral sites. In this study we focused on the relations between charge density and the onset of collapsing layers. It is known that treating clay by the Hoffmann Klemen procedure may induce collapsed layers. Various low charged montmorillonites were investigated and collapsed layers were detected by XRD. Our results show that collapsed layers have significantly increased with clays which have CEC lower than 65mmol/100g swelling clay corresponding to a charge density of 0.24 charges/ half unit cell. After the Hoffman Klemen treatment, the CEC of the swelling fraction can be estimated by dividing the measured CEC by the portion of swelling clays in the sample. The results suggest a CEC value of 65mmol/100g clay to be the lowest CEC of a completely swellable clay. Further experiments are addressed to explain this important phenomena of a swellable clay.

STILPNOMELANE-MINNESOTAITE-GREENALITE MINERAL ASSOCIATION IN THE MORAVIAN DEVONIAN (CZECH REPUBLIC)

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The Devonian Vrbno Group in the Jeseníky Mts. is noted for the occurrences of ferrous and non-ferrous metals. The former continue in the buried área of the Upper Moravian Basin where they were exploited. The results of the mineralogical investigation of reported iron-bearing phyllosilicates are discussed. The deposits of these iron ores are associated with the volcanism and the submarine hydrothermal exhalations. Attention was paid to the occurrence of the interesting stipnomelane -minnesotaite -greenalite mineral assemblage of this área which resembles that described from the iron- ore formation of the Mesabi Range, Minnesota. These Fe-phyllosilicates were submitted to the laboratory examinations. X - ray diffraction methods, chemical examination, thermal analyses, and measurements of the refractive indices were used. As to their crystal structure stilpnomelane, greenalite, and minnesotaite are supposed to belong to modulated layer silicates.

Stilpnomelane forms acicular crystals with their fan-shaped arrangement. In some places stilpnomelane flakes with distinct cleavage are bigger. Sometimes this mineral forms lats-shaped and sheaf-like aggregates. From the chemical point of view stilpnomelanes differ from chlorites mainly by their higher SiO_2 and Fe_2O_3 amounts and lower amouts of Al_2O_3 and H_2O. Minnesatoite was found in the compact dark-grey rock densely interweaved with light glassy parts of yellowish green matter. Under microscope colourless sheaf-like and fan-shaped aggregates with higher birefringence are observable. Minnesotaite was previously considered as ferrous iron analogue of talc. Greenalite is dark green, finely grained mineral which in the rock forms a network between sheaf-like aggregates of colourless minnesotaite. It was classified as Fe^{2+} serpentine.

INFLUENCE OF ORGANIC MATTER ON SMECTITE ILLITE TRANSFORMATION IN CARBONATES

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The effect of organic matter on the transformation of smectite to illite is still controversial. Some authors postulate an acceleration of the illitization process in presence of organic matter, for others organic matter inhibits illitization.

This study concentrates on the expandibility behaviour of illite-smectite mixed layers from alternating organic-carbon rich sediments and organic-carbon poor sediments. For this purpose three weakly metamorphosed Early Cretaceous sedimentary sequences located in different basins of the W-Tethys Ocean realm were investigated. All sedimentary sequences are characterized by a transition from pelagic limestones to hemipelagic marly limestones and marls which are alternated with black shales (<11 wt.-% organic carbon). The onset of the hemipelagic serie is characterized as a 2-5m thick organic matter rich sequence of siliceous limestones and shales known as "Livello Selli" (Oceanic Anoxic Event 1a). Each section shows a different thermal history and various amount of carbonate in the "Livello Selli".

The clay fraction consists of 1M/1Md illite, Fe-poor chlorite, random ordered (in one section ISI-ISII-ordered) illite smectite mixed layers, biogenic quartz and Na-rich feldspars. Illite-smectite mixed layers of black shales show smaller amount of expandable layers (up to 30%) than those from organic-carbon poor sediments. However, the difference in expandibility in sediments with different amount of carbonate and organic-carbon of the "Livello Selli" is not so pronounced.

The results suggest that a primary, detrital origin of the illite-smectite mixed layers causes the differences in expandibility values.

A COMPARISON OF FUNCTIONALIZED CLAYS AND MESOPOROUS MOLECULAR SIEVES FOR ENVIRONMENTAL REMEDIATION APPLICATIONS: ADSORPTION OF HEAVY METAL IONS

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High surface área oxides, including clays, have been widely considered for the removal of toxic compounds from the environment. Clays functionalized by the intercalation of surfactants or by the interlayer grafting of sulfhydryl ligands have been shown to have strong binding affinities towards organic pollutants and heavy metals, respectively. In recent years, the discovery of Mobil M41S molecular sieves oxides with well-defined mesoporous channels (with pore diameters between 20 and 100 Å) has provided a revolutionary new outlook in the field of nanoporous technologies. Following chemical treatments similar to those used for the preparation of clay-based adsorbents, the functionalized derivatives of mesoporous molecular sieves have resulted in the preparation of highly effective adsorbents for both heavy metals and organic pollutants. The goal of this presentation is to compare the merits and disadvantages of both layered silicates and mesoporous molecular sieves as they pertain to environmental remediation technology. This comparison will be illustrated by the characterization and heavy metal ion adsorption affinity (particularly towards Hg and Pb) of materials prepared by the grafting of thiol functionalities to the surfaces of both H-exchanged montmorillonite and mesoporous molecular sieves (HMS and MCM-41). The implication of these observations on the future of clay chemistry for environmental remediation will also be discussed.

CONTROL OF SITE POPULATIONS AT SYNTHESIS, BY INTER-SlkHEET DIFFERENTIAL THERMAL EXPANSION IN A T-04O-T LAYER SILICATE

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Due to structural constraints involving long range layer misfit and short range bond matching, ideal end-member annite is never synthesized. Instead, the constraints are satisfied by both non-destructive partial oxydation (via H-loss) of the Fe^{2+}, and Fe^{3+}-Al^{3+} exchange between the octahedral and the tetrahedral sheets. We measured Fe^{3+} site populations in nine annite specimens synthesized using the C-CH_4 and Ni-NiO buffers, and various equilibration temperatures. The measurements were performed using the most recent Mössbauer spectroscopy data treatment and spectral analysis methods[1]. These include (1) analytic methods for removing the spectral distortions associated to the effects of absorber thickness and (2) a Voigt-based fitting method that allows arbitrary-shape quadrupole splitting distributions for each site. We obtained site population measurements with precisions of 0.2-1 % of total Fe. By using equilibration temperatures over the entire stability range for annite, we have traced the evolution of the octahedral and tetrahedral Fe^{3+} site populations and have obtained an experimental lower bound on Fe3+/Fe. Also, we observed a migration of the Fe3+ ions from the tetrahedral sites to the octahedral sites with increasing equilibration temperatures. These results are best understood in terms of inter-sheet differential thermal expansion, in the context of a structural misfit model that also includes tetrahedral sheet rotation and a cation size dependent octahedral flattening.

[1] Rancourt, D.G. et al. 1994. Phys. Chem. Minerals 21: 244--249, 250--257, 258--267.

QUADRUPOLE SPLITTING DISTRIBUTIONS OF LAYER SILICATES FROM MÖSSBAUER SPECTROSCOPY

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Given recent advances in Mössbauer spectroscopy methodology (Rancourt et al., 1994), it has become possible to extract intrinsic quadrupole splitting distributions (QSDs) from Fe-57 Mössbauer spectra. Such QSDs are directly related to probe local environment populations, that is, to populations of crystallographic or chemical or distortion local environments, depending on the dominant mechanism that causes variations in hyperfine electric field gradients in the particular mineral sample. For example, in layer silicates, octahedral cis and trans site populations can sometimes be measured (e.g., in certain muscovites, Shabani et al. 1997) or populations in various nearest neighbour anion coordinations (e.g., in annite- fluorannites, Rancourt, 1997) or populations in various local distortion environments (Rancourt et al. 1994). In this contribution, we present measured QSDs from several new synthetic solid solution series including Al-deficient, Al-normal, and Al-rich phlogopite-annites. We compare these to the QSDs from other solid solutions and give crystal chemical interpretations based on the known structures and stoichiometries.

Rancourt et al. (1994) Phys. Chem. Minerals 21: 244-249; 250-257; 258-267.

Shabani et al. (1997) Proceedings of ICC'97.

Rancourt (1997) Proceedings of ICC'97.

CLAY MINERALOGY OF CANADIAN SOILS

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This paper presents a comprehensive summary of information regarding mineral transformation and translocation in the clay fraction of Canadian soils. Since the first report of clay mineralogical data for Canadian soils by Clark et al. (1937), many papers have been published on subjects related directly or indirectly to the mineralogy of the clay fraction. The majority of Canadian soils have been developed after retreat of the last glaciation some 12,000 years ago. A cool climate under which Canada has been subjected has allowed for limited alterations of minerals in pedons. Among eight inorganic soil orders of Canada, only Podzolic soils that have been developed under relatively high precipitation and well-drained conditions show distinct mineral transformations. In the Podzolic soils, chlorite disappeared or diminished in surface horizons, and mica and possibly some chlorites were transformed by hydration into partially or fully expansible clay minerals. Allophane, imogolite and ferrihydrite appeared as pedogenic minerals in surface horizons of some Podzolic soils. In soils which belong to other orders, virtually no or limited alterations occurred such as a partial hydration of mica and chlorite minerals. Paleosols are sporadically distributed in Canada. In these soils, kaolin minerals are major constituents in the clay fraction in association with a lesser amount of gibbsite. This indicated that some parts of Canada had once been subjected to strong weathering conditions in pre-Wisconsinian time. An alphabetical list of minerals occurring in the clay fraction of Canadian soils will be provided for quick references.

OIL SANDS TAILINGS RECLAMATION VIA MANIPULATION OF CLAY BEHAVIOUR

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During deposition of oil sands extraction tailings in the recycle water ponds, the coarse sand separates from the fine clays and over a period of time, the fine clays sediment to a 30% solids material known as mature fine tailings. Although the fraction of the tailings stream that becomes mature fine tailings is relatively small, since the start of commercial operation, it has accumulated to over 300 million cubic meters, and at current production rates will be over one billion cubic meters by the turn of the century. Direct observations of the clay floc structure in mature fine tailings using cryogenic scanning electron microscopy, conventional optical and confocal laser scanning microscopy, were correlated to the bulk rheological properties and with the degree of dispersion of the clays in suspension. Aside from the relatively subjective microscopic observations, a novel method based on the amount of light reflected from clay flocs was used to quantify the degree of flocculation and relate it to changes in water chemistry and in the bulk behaviour of the clay suspension. The ability to chemically manipulate the clay floc structure and influence bulk behaviour in order to create a clay tailings that can be economically reclaimed was demonstrated on a fundamental level using these techniques. This fundamental understanding of the flocculated clay structure has led directly to the development of the consolidated (or composite) tailings process (undergoing commercial trials at Suncor) which can result in a dry landscape reclamation of the mature fine tailings.

CLAY MINERALS IN DEEP SEA MUD (l0,898m depth) FROM THE MARIANA TRENCH

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A deep sea mud was collected from a depth of l0,890m at the Mariana Trench by "KAIKO", Japan Marine Science & Technology Center (JAMSTEC), under the following conditions. It is the first material obtained from one of the deepest sea points in the globe. Collection conditions were: By the "KAIKO" an unmanned submersible; Submarine voyage No. 21; Date: 29 February, 1996; At the depth of 10,898 m, the Challenge Sea Region, the Mariana Trench (1122.10'N, 14225.85'E); Temperature: 2.6C, Pressure: about 110 Mpa. Dark gray mud suspended in sea water is tested by means of X-ray powder diffractometry and then is washed of NaCl by distilled water and tested by the same methods. Clay material and sandy part in the washed mud are separated by means of decantation method.

The clay materials are composed mainly of chlorite (iron rich member), montmorillonite, and associated with micaceouse clay mineral, kaolin mineral and a small amount of some another clay mineral (supposed as tosudite). Some amorphous material was also present. The sandy part is composed of plageoclase, chlorite and montmorillonite, and associated with quartz, alpha-cristobalite, clay minerals, etc. These minerals assemblages are observed in the physical conditions as mentioned above. In the mud, fine organic materials, many fragments of sponge spicules and a few siliceous skeletons such as radiolarians and diatoms are also observed under the microscope. Chemical analysis of the clay material shows Fe2O3:8.41 MnO:0.85 wt.% as the main composition of the amorphous material.

MODERATION OF SILICA BIOLOGICAL ACTIVITY

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Two phases of silica, crystalline quartz and non-crystalline opal, often occur in clay and other sedimentary deposits. Crystalline phases of silica can exhibit biological activity, ranging from pronounced to very little, whereas non-crystalline phases exhibit very little. The reasons for these differences become important in view of recent regulatory actions that acknowledge them. Some of the major factors in fresh quartz surfaces include the orderly crystalline arrangement of atoms, the hydrophilic-hydrophobic character, the broken Si-O bonds that can generate hydroxyl and oxygen radicals, an openness that might shelter undesirable molecules and trace impurities. As quartz ages, its surface becomes disrupted and its biological activity declines. The more random structure, the elimination of broken bonds through hydrolysis and other factors contribute to the decline. The direct interaction of silica particles with lung epithelial cells and the fate of macrophage scavenger cells that engulf silica particles can elucidate these changes in the crystalline silica phases.

MINERALOGY AND GEOCHEMISTRY AS INDICATORS OF PROVENANCE AND DEPOSITIONAL ENVIRONMENT IN CLAYS: THE PELITIC LEVELS IN THE CRETACEOUS APULIAN CARBONATE PLATFORM, SOUTHERN ITALY

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In the current study, the mineralogy and the geochemistry of clays have been checked to constrain both provenance and depositional environment. A set of twelve samples, coming from pelitic levels interbedded in Cretaceous limestones of the Apulian Carbonate platform (southern Italy), has been studied. The samples are grouped into four subsets corresponding to distinct stratigraphic settings. Bulk samples have been analyzed for mineralogy (XRD, SEM-EDX) and chemistry (INAA, AAS, XRF). In order to get constraints for mineralogical and grain-size control on selected trace elements, size fractions of four selected samples were also analyzed and a mass balance calculation performed. Our major tools allow us to discriminate the analyzed clays: 1- the mineralogical assemblage of the bulk samples. The subsets are either kaolinite-dominated or smectite + illite-dominated; 2- The chemistry of illite and smectite; 3- The distribution of selected trace elements. The discrimination is mainly linked to both high field strength elements (HFSE: Y, Zr, Nb, RareEarth Elements) and transition elements (TEE: V, Cr, Co, Sc); 4- The mineralogical and grain-size control on the distribution of selected trace elements. In the kaolinite-dominated subset, for instance, selected trace elements are mostly controlled by accessory phases concentrated in the 32-64 m grain-size fractions. On these bases we can both individuate parental affinities and distinguish continental clays from marine clays. The differences are related to different tectonic settings and are consistent with the evolution of the Tethyan ocean during the Cretaceous age.

SOIL MINERALS AND SOIL ORGANIC MATTER DYNAMICS IN AGGREGATE FRACTIONS OF A GLEYSOLIC SOIL

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We examined the influence of particle architecture and minerals of soil aggregates on soil organic matter (SOM) content and its dynamics. Macroaggregate (> 250 m), microaggregate 1 (50-250 m) and microaggregate 2 (< 50 m) fractions of adjacent forested and cultivated Gleysol were obtained by wet sieving. Aggregates and respective clay fractions were characterized using optical, X-ray diffraction, chemical and physical analysis. SOM dynamics was defined using radio carbon dating and the natural abundance of 13C. Microaggregate 1 had primary particles with the largest mean equivalent spherical diameter (ESD), void volume, microbial biomass (MB) and SOM content of all aggregate fractions. Soil organic carbon (SOC) content and MB in aggregates was associated with particle mean ESD, ammonium oxalate extractable Al, chloritized vermicultite and vermiculite. The mean residence time (MRT) of SOC in macro and microaggregate 1 was <100 y, and that of microaggregate 2 was 395 y. Turnover time of SOC was 14 y in macroaggregate, 61 y in microaggregate 1 and 275 y in microaggregate 2. We concluded that the mean ESD and expandable phyllosilicates of aggregates influenced living habitats and thus SOM dynamics by providing different void and protective space, and influencing SOC supply for soil microorganisms.

STRUCTURAL STUDIES OF HYDROXY-Ga PILLARED CLAYS BY Ga K-EDGE AND Si K-EDGE X-RAY ABSORPTION SPECTROSCOPY

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Pillared clays, obtained by exchange reactions of smectite with polycations, can be used as catalysts or adsorbents. The most commonly used pillaring agent is the Al13polycation, with the following structure : twelve octahedra surrounding a central aluminum tetrahedron. To improve the adsorption capacities of Al13-pillared clays towards organic pollutants, organic polymers can be cointercalated. The synthesized materials are aged or/and calcined at 500°C. Taking advantage of the structural analogy between Ga13 and Al13 polycations, the local structure of these materials can be investigated by X-ray absorption spectroscopy (XAS). These experiments were carried out at the Ga K-edge and at the Si K-edge on gallium pillared montmorillonites and saponites. Ga K-edge experiments showed that intercalated Ga13 polycations keep their initial structure. The cointercalation of organic matter does not lead to any structural modification. Ageing results in structural changes revealed by a smaller number of Ga neighbours, this phenomenon is fully prevented when polymer is cointercalated. After calcination, distance distribution curves show that : (i) the signal intensity is strongly reduced, (ii) the peak assigned to GaVI-GaIV distance disappears. Si K-edge experiments are more difficult to interpret because of the low amount of Ga atoms per unit cell of clay. However, calcination appears to provoke some noticeable differences on the Fourier transforms. As a complementary technique to more classical methods (XRD, nitrogen adsorption volumetry...), XAS appears as a very powerful tool to investigate the structure of the pillars.

STRATIGRAPHY AND MINERALOGY OF RED-PURPLE CONTINENTAL SEDIMENTS, ALTER DO CHÃO FORMATION OF MANAUS, BRAZIL

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One of the greatest kaolin deposits of the world is associated with the Alter do Chão sediments which occur in the medium and lower Amazon basin. In the region of

Manaus, the red and purple color of these late Cretaceous sediments can be related to continental erosion of a previous ferralitic materials formed under warm, humid and well drained conditions. At the margin of this region, a generalized groundwater aquifer has bleached the sediments and led to the formation of kaolin deposits. The objective of this study was to use mineralogical and geochemical tracers in order to (i) characterize the red-purple sediments for further comparison with the kaolin deposits and (ii) highlight the main sources and cycles of erosion. A 35m thickness cross section of the Rio Negro bank was investigated using field characterization, micromorphological techniques, mineralogical and geochemical analysis (XRD, EPR; TEM, SEM; ICP). The kaolinite of the red-purple sediment is poorly crystallized (average [001] MCD size = 150Å) while the one in the associated white kaolin layers presents a better crystallization. In these bleached layers, higher MCD size (average [001] MCD size = 200Å) suggests recristallization of kaolinite. Two sedimentary sets of different origin, separated by a paleosol, were differentiated. According to the high cerium/lanthanum ratio (average Cepaas/Lapaas = 7.25) of the lower set, its origin can be related to the erosion of cerianite rich soil materials coming from the close Precambrian shields.

IDENTIFYING THE VARIABLES IN DIAGENETIC CHLORITIC CLAY MINERALS OF SILICICLASTIC RESERVOIR ROCKS

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The bad news is that peak intensity relations of the basal series (00l) of diagenetic chloritic clay minerals in XRD tracings can vary for at least six reasons: 1) trioctahedral hydroxyl sheets combined with either trioctahedral or dioctahedral 2:1 layers; 2) the degree of completeness of the hydroxyl layer; 3) the degree of symmetry of the distribution of heavy (e.g., Fe) ions between the hydroxyl interlayer sheet and those of the 2:1 layer; 4) presence of epitaxially intergrown, expandable layers; 5)presence of epitaxially intergrown, 7Å layers; and 6) the amount of Fe and Fe-like ions in the octahedral sites. For quantitative or qualitative work with chloritic clay minerals, these variables must be taken into account. Modeling the 00l series of peaks with NEWMOD=AE, using sequential dissolution to isolate chemical components, and step heating experiments to degrade structural units, some of these variables can be generalized. Two examples: two Mississippian reservoirs can be statistically distinguished based on characteristics of contained chloritic minerals; and linear decrease in 7Å layers intergrown with chlorite with increase in depth. The good news is that with so many complications, diagenetic chloritic clay minerals must hold a great deal of information on the history of the sediments within which they are found. Now, the obvious task is to begin to decipher whatever it is they have to tell us.

INCIPIENT VERMICULITIZATION PROCESSES IN BIOTITES OF THE OLIGO-MIOCENE OF THE NORTHERN APENNINES (ITALY)

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Three purified biotite populations have been studied in order to define the crystallographic parameters of biotites at an intermediate alteration stage (average K2O% between 5.3 and 5.6). Samples come from marine Oligo-Miocene volcaniclastic sediments of the Northern Apennines. After a multiple purification procedure, completed by hand picking, the samples have been analysed by diffractometric (XRD), thermal (TG, DTG, DTA), chemical (XRF, AAS, selective electrode) methods. Microscopic observations (SEM-EDS and optical) were used for isolated flakes.

The biotite populations show heterogeneous compositions within the same sample (SEM-EDS control), but considering the results from the separates (i.e. averaged values) samples show different degree of vermiculitization marked by progressive depletion of Fe+2, K, Mn, Ti, Ba, Rb, Cl, Zr, Y and Sc and enrichments of Fe+3, Cr, Co, Cu and V. The transformation proceeds through the oxidation of some Fe+2 that causes the loss of K and the increase of H2O into the interlayer zone. The transformation is more intense in biotites with lower Fe, Ti, Mn and with higher content of Zr, Sc and Y (accessory inclusions), that likely crystallized at higher temperature. The distribution of Fe+2 and Mg is ordered on the XY plane, the Mg being more abundant along the ao axis and the Fe+2 along the bo. The oxidation of Fe+2into Fe+3 caused a decrease of the OH--structure bonds energy, changing the temperature of the dehydroxilation reaction at about 600°C. Taking into account the effect of vermiculitization, the composition of parent magmas has beeen supposed.

NON-STOICHIOMETRY IN NATURAL GOETHITES

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At Earth surface, goethite is a ubiquitous iron oxyhydroxide which may mainly incorporate aluminum and excess structural water in its structure. Non-stoichiometric protons compensate the charge of trivalent cation vacancies and are responsible for an increase of the a-cell-parameter. Indeed, it is now generally accepted that the actual structural formula of goethite should be written as (FexAl1-x)1-y/3 O1-y(OH)1+y. New data will be presented on the crystal-chemistry of natural goethites originating from contrasting environments: a bauxite ore from Guinea and lake bottom sediments from Finland. Those are compared with synthetic Al-goethites grown in controlled conditions. Rietveld analysis of cell parameters and site occupancies, as well as Mössbauer measurements of Néel temperatures, evidence that non-stoichiometry increases with Al-substitution and mainly depends on growing kinetics. Despite their high Al-substitution, goethites in the bauxite studied are the most stoichiometric among all natural and synthetic goethites studied. That may result from low nucleation rates and slow crystal growth, limited by low solubility of Fe3+-bearing precursors in the oxidizing and slightly acidic conditions prevailing in the unsaturated zone of tropical soils. In contrast, despite their low Al-substitution, goethites from Lake sediments are characterized by high cation deficiency. That may be related to high nucleation rates resulting from oxidation of high amounts of dissolved Fe2+ at the water-sediment interface. In the future, sensitivity of non-stoichiometry in goethites to formation conditions could be used to trace paleoenvironments.

MÖSSBAUER MINERALOGY OF LUNAR SOILS, MARTIAN METEORITES, AND MARTIAN ANALOGUE SOILS

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Iron is particularly important for exploration of planetary surfaces because it is abundant and multivalent (primarily 0, +2, and +3). Knowledge of its oxidation state and distribution among iron-bearing mineralogies (Mössbauer mineralogy) constrains the types of materials present on planetary surfaces and permits inference of processes that formed and subsequently modified them. Lunar soil is formed predominately from impact comminution of rock. The particle size distribution is approximately log normal with <1% of the mass in the clay size fraction. Iron is present mostly as Fe2+ in olivine, pyroxene, glass, and Fe-Ti oxides. Up to ~1%

nanophase metallic iron is also present. Phyllosilicates are absent. The Mössbauer mineralogy of the 12 Martian meteorites is dominated by Fe2+ in pyroxene, olivine, and Fe-Ti oxides. Three have in addition nanophase ferric oxide (ferrihydrite?). Spectral analogues of the Martian surface include oxidatively-altered impact-melt rocks and volcanic tephra from Hawaii. For impact-melt rocks, alteration occurred during late-stage crystallization and subsolidus cooling of the impact melt by oxidizing fluids while the rocks were still hot (250-900C). The Mössbauer mineralogy is dominated by Fe3+ in hematite and nanophase oxide and Fe2+ in pyroxene; low-iron phyllosilicates are present. Altered volcanic tephra includes palagonitic tephra (from low-temperature alteration of volcanic glass) and sulfate-bearing tephra (from acid-sulfate weathering). The Mössbauer mineralogy of the former is dominated by Fe3+ in nanophase ferric oxide and the latter by Fe3+ in jarosite. Phyllosilicates do not appear to be present, and the clay size fraction is 2-5%.

UNDESTANDING IRON TRANSFER IN RIVERS: CASE STUDIES FROM TROPICAL ENVIRONMENTS

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The objective of this paper is to determine whether the status of iron in transported sediments reflects weathering and erosion processes occurring at different scales. Emphasis will be put on transfer of iron in tropical environments, on account of Fe-oxides abundance in weathering crusts and their role in partitioning elements between dissolved and solid loads. Two sampling sites have been selected for this study: (1) a small catchment (1 square km) located in Cameroon; (2) the Oubangui river basin which drains an área of 0.5 million square km. Suspended matters have been characterized with XRD, FTIR and TEM methods. Diffuse reflectance [1] and electron paramagnetic resonance (EPR) spectroscopies [2] have been used to investigate the status of iron. Due to their high sensitivity and their structural selectivity, these spectroscopies gave an accurate picture of the distribution of Fe(III): (i) in particulate fraction, Fe is located in kaolinite phase and closely associated Fe oxides; (ii) in colloidal fraction (< 0.2µm), Fe(III) is adsorbed on organic matter in inner-sphere complexes and forms Fe-gel-like phases. The distinction between inherited and neoformed Fe-bearing phases and the important role played by organic matter in the mobilization of iron is emphasized at local scale. Furthermore, it will be demonstrated at regional scale that Fe-oxides are good tracers of suspended sediments origin according to the season.

[1] Malengreau et al. (1994) Clays & Clay Minerals 42, 137-147.

[2] Muller et al. (1995) Amer. J. Sci. 295, 1115-1155.

CLAYS AND CLAY MINERALS: WHAT CAN MÖSSBAUER SPECTROSCOPY DO TO HELP UNDERSTAND THEM?

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Following the first work on clay minerals some 30 years ago, Mössbauer spectroscopy has been repeatedly applied to the characterization of minerals formed in the weathering environment. Studies involving clay minerals sensu stricto, i.e. phyllosilicates, have concentrated on the oxidation state of iron and structural site occupancies and distortions. Recent work involving high-quality data has shown that previous cis and trans OH-sites assignments are often not tenable. The study of minerals of this group is often hampered by several facts: they are generally not monophase, they may be poor in iron leading to low count rates and adverse effects such as slow paramagnetic relaxation and only few iron-rich species order magnetically above 4.2 K. Mössbauer spectroscopy can also be used to follow the transformations that take place during clay firing (e.g. during the production of structural clay products) but, because of the paucity of data on monomineralic clays, the firing behaviour of most clays is at present often understood only qualitatively. Mössbauer data on iron oxides are generally more straightforward because these can all be studied in the magnetically ordered state, thus providing additional parameters. A further advantage of Mössbauer spectroscopy when studying these minerals lies in its high sensitivity for magnetically ordered phases. Adverse effects ensuing from small particle size, interparticle interactions, non-stoichiometry and foreign element substitution that often affect the Mössbauer parameters of iron oxides occurring in clays and soils can be partly or completely offset by taking Mössbauer spectra at low temperatures.

MORPHOLOGY OF AUTOGENOUS SILICA MINERALS (OPAP-CT AND QUARTZ) IN THE TERTIARY CLAYEY SEDIMENTARY ROCKS FROM THE OGA PENINSULA, AKITA, JAPAN

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Prograde evolution of smectite and silica minerals occurring in the sedimentary rocks which are called "hard shale' of the Miocene Onnagawa Formation in the Oga Peninsula, Akita, Japan, has been studied using XRD and SEM. This formation, which is composed of rhythmic alternation of siliceous mudstone and smectitic claystone, is originally deposited by turbidity current, and therefore has uniform composition primarily. As the result of diagenesis, at the present time, this formation divided into three zones in terms of alteration of silica minerals, namely opal-A, opal-CT, and quartz zones. Observation on the continuous change of morphology of autogenous silica minerals accompanying with transitions from opal-A to opal-CT and opal-CT to quartz is the point that weighs with this study, especially transition zone between opal-CT and quartz can be seen at one outcrop. Sudden disappearance of opal-CT at near quartz zone suggests that the dissolving of opal-CT occured rapidly, and therefore determination of strict conditions for this transition is possible from the observations of their morphology and the association of minerals. This paper discusses details about the change of the morphology of autogenous silica minerals and other minerals, including potassium feldspar and pyrite, occurring in these transition zones by SEM observations and the role of the examined clay mineral as agent for dissolving and precipitating of silica minerals in diagenesis.

HRTEM ON SMECTITE TO CHLORITE REACTION

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The microstructures of interstratified minerals such as chlorite/smectite and illite/smectite provide us with important information on the processes and mechanisms of the formation reactions of the product minerals. HRTEM is a powerful technique to examine the microstructures of interstratified minerals. We examined the process and mechanism of the reaction of smectite to chlorite by HRTEM with proper image interpretation. Volcaniclastic rocks containing mixed layer samples were collected from Kamikita, northern Japan. The samples of <1 m fractions containing 80%, 50%, 40%, and 0% smectite (by XRD) were resin impregnated and then *ultramicrotomed for TEM observations. Under a proper underfocus condition (about - 100 nm), thick, black fringes correspond to 2:1 layers, thin, black fringes to hydroxide sheets, and interlayers to white fringes. Corrensite grows in a smectite domain of 10 - 30 nm thick forming a domain of 5 - 10 nm thick. Single chlorite layers inserted in smectite layers or irregularly interstratified structure of chlorite/smectite or corrensite/smectite did not occur. In the middle stage of the reaction, only aggregates of corrensite 5 - 15 layers thick were observed; discrete chlorite 2 to 3 layers thick was found occasionally. In the last stage, chlorite 10 - 30 layers thick was the predominant phase. The HRTEM observations indicate that, in the smectite to chlorite reaction, (1) corrensite and chlorite grow as isolated domains in host smectite and corrensite, respectively, (2) regular R=1 is the only interstratification, and (3) dissolution and crystallization are the formation mechanism of corrensite and chlorite.*

CLAYS FOR OUR FUTURE

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Clays have been important ever since the first records of human existence were documented. As our standard of life has increased over these eons of time, the use of earthen materials has increased. In the twentieth century, the use of clays and clay minerals has multiplied extensively. This is particularly true of those clays that were produced from essentially monomineralic deposits or could be beneficiated to produce dominantly monomineralic products. Today, kaolins, bentonites, and hormites have over a hundred documented uses. Each and every day most everyone uses at least some item that contains a clay material. What will the twenty-first century bring regarding the utilization of the exciting minerals we know as clay minerals? With the continuing improvement of analytical equipment and methods, our knowledge of the physical and chemical properties of clay minerals will become even more refined. Improved mining and processing technology will permit the production of new and improved products. Chemically modified clays that change surface properties will open the door to many new uses as well. Absorbent and adsorbent clays will play a more significant role in the protection of our environment. Pillared clays for special catalysts and sorbent applications will become more important. And, the new technology using clay minerals in nanocomposites will expand. Specific examples of recent technological developments that will enable clays to grow in importance in our future will be discussed.

THE FUNDAMENTAL PARTICLE MODEL: A CLAY MINERAL PARADIGM

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In a series of papers published from 1982-1987, researchers from the Macaulay Institute, Aberdeen, Scotland, presented a radical model for the interpretation of the crystal structure, chemistry, and genesis of interstratified clays. The model reconciled electron microscopy and X-ray diffraction (XRD) analytical data from a variety of sedimentary clay specimens, and proposed that these minerals were composed of micro-crystalline fundamental particles whose adsorptive interfaces were responsible for the expanding smectite layers observed by XRD. The term interparticle diffraction was used to describe this phenomenon.

GROWTH KINETICS OF GIBBSITE IN KAOLINITE POWDERS

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Growth and dissolution relationships between gibbsite and kaolinite are key to understanding weathering processes that lead to laterite and bauxite formation.
Absolute rates can be obtained, and reaction mechanisms can be inferred, from stirred-flow reactor experiments on mineral powders. However, details of epitaxial
relations and the kinetic controls exerted by the mineral/fluid interface cannot be discerned. Furthermore, identification of the growth phase typically is based only on
changes in solution composition. We grew gibbsite on kaolinite powders at 80°C, pH 3 under variable saturation state conditions with respect to both phases.
Verification that the growth phase is gibbsite has been made by rotating anode X-ray diffraction. Quantification of gibbsite by solution concentration changes and by
comparison of the XRD patterns with standard mixtures yields consistent results. In addition to identifying the growth phase (typically less than or equal to 1 wt.% of
the total mass of material), XRD data can provide information on the epitaxy between gibbsite and kaolinite and on the gibbsite domain size. Examination of
previously-obtained experimental run products shows that gibbsite forms when kaolinite dissolves incongruently, i.e. when dissolved Si/Al is greater than 1. Finally,
the XRD results demonstrate that gibbsite may be more stable than boehmite at 80°C, or that gibbsite nucleates more easily than boehmite in the presence of
kaolinite. This research was sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences/Geoscience under contract DE-AC04-94AL85000 with
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ALLOPHANE AND SMECTITE AS MACROMOLECULES

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Dilute suspensions of allophane and montmorillonite form cells, membranes and fibers, when organic solute such as ethanol is gradually dissolved in the suspensions.
Those are all stable only in water mixed with ethanol, and, thus have to be observed by optical microscope in the liquid. Similar suspension of iron-removed
allophane forms dendrites, needles and aggregates of non-cubic crystals. They are also stable only in the liquid. The behaviors of the suspensions indicate (1) that
such clay minerals are in organic macromolecules in suspension rather than crystal fragments, (2) that there may be a world of inorganic crystals stable only in water
of limited conditions, and (3) that they might form precursor of living individuals in the inorganic world of the prebiotic Earth.

STEREOSPECIFIC INTERCALATION OF -AMINO ACIDS INTO AN ANIONIC CLAY COMPOUND

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In the chemical evolution on primitive earth led to the origin of life, a great preponderance of L-amino acids and D-saccharides is still remained as an enigma. As one
of the reasons, a stereo selective adsorption by clay has been proposed, but definite evidence for this postulate could not be obtained so far. Here we report the
extraordinary intercalation behavior of -amino acids such as phenylalanine (Phe), leucine (Leu) and histidine (His) by the Zn-Al oxide solid solution powder prepared
by the calcination of a synthetic Zn-Al carbonated layered double hydroxide (LDH), ZnAl(OH)(CO)0.50HO (anionic clay compound). When the oxide was mixed
with each enantiomers solution or racemic solution of the amino acids at 25 Äü, the oxide was found to incorporate the amino acid and water molecules with
reconstructing the original LDH-type structure. In neutral or weakly alkaline solutions, the amino acids seemed to be intercalated as an associated form of few
molecules in the gallery of the resulting LDH, in which the 2.0-2.7times amount for the theoretical intercalation capacity for univalent anion has been intercalated. In

the case of Phe,the basal spacing of the solid product was expanded to 16.5-16.9Å from 7.7Å of the parent LDH. The most interesting result was that when the racemic solution was passed through the column packed with the oxide powder, the specific optical rotation of the eluate showed minus values of maximum about -4°,which means the preferential intercalation of D-Phe in the gallery of the LDH. The reason for the results is unclear, but they indicate the possibility of the optical division of -amino acids by natural anionic clays on primitive earth.

RAMAN MICROSPECTROSCOPY - A RAPID METHOD FOR MINERAL CHARACTERISATION AND IDENTIFICATION

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Raman microscopy in the past has been an expensive and difficult technique to use for the analysis of minerals. In the past few years various technological advances have completely changed this view of the method, to the extent that it has become very affordable and user friendly. This paper will focus on these recent technological advances and illustrate the application of Raman spectroscopy in the fields of clay mineralogy, general mineralogy, and gemmology. The latter of these applications has had a very large impact in may gemmological laboratories. Over the past two years gemmological testing laboratories in India, Thailand, Switzerland and Italy are routinely using the method for the identification of mineral inclusions held within gemstones. The attributes of the Raman microscope approach to sample analysis are: 1m diameter sample size (picogram quantity of sample), no sample preparation, non-destructive confocal (i.e., can analyse sub-surface material), and rapid data collection times (seconds) are used to their full effect. Recently, Frost et al. have shown the method to be very useful in the identification and structural analysis of clay minerals. An investigation of kaolinite, halloysite, dickite and nacrite revealed unique Raman data. The ability to investigate a single crystal and obtain orientational information has been cited as important. As an aid to mineral identification a comprehensive database has been prepared for the non-expert.

STRUCTURAL AND TEXTURAL CHARACTERIZATION OF A VULCANIC GLASS WITH CLAY INCLUSIONS

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The studied sample consists on a vitreous material of vulcanic origin, with crystalline inclusions of smectitic nature, proceeding from Moa (Holguín, Cuba). Previous analysis of analogous materials from the same área indicate the presence of montmorillonite, calcite, quartz, other silicates and amorphous glasses. The statement of the composition of the inclusions was performed by powder X-ray diffraction analysis by using as reference materials an illite-smectite mixed-layered material from the Ore Mountain basin, a regular mixed-layered mineral from a disposal site in the Röt formation (Thuringia) and the HCl-insoluble residue of an Ore Mountain dolomite-calcite marble, consisting of mica and chlorite minerals as well as quartz. Results of analysis showed the presence of calcite, albite, opal and a di-octahedric three layer silicate (montmorillonite group). Thermogravimetric analysis of various fractions of this material, with different particle size, showed a weight loss of about 15% (associated to the water elimination) below 900 K. The DSC corresponding curves were also obtained, indicating the presence of two or three stages *associated with endothermic peaks. EGA-MS analysis are also performed. The textural characterization was achieved by N_2 adsorption at 77 K. The resulting isotherms were of IV type, showing a marked hysteresis loop indicating a well-developped mesoporous texture. Analysis of these isotherms was performed by several methods.*

SYNTHESIS AND CHARACTERIZATION OF LAYERED METAL HYDROXIDES

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Layered materials that are able to exchange interlayer ions for inorganic or organic ions have attracted considerable attention. Through the incorporation of a guest species into a layered host, novel solids may be engineered with desirable physical and chemical properties. Here, we compare two closely related types of layered materials, consisting of positively charged brucite-like layers and interlayer charge-balancing anions (I) Layered double hydroxides (LDHs) and (II) Zinc basic salts.
(I) LDHs have the general formula $[M(II)_{1-x}M(III)_x(OH)_2]A_{x/n}.mH_2O$, where M(II) and M(III) are divalent and trivalent metal cations, respectively and A is an anion of charge n incorporated between the layers. An extensive choice of matrix ions and gallery species is available; therefore a rich variety of materials may be synthesized. Here we study the direct synthesis of a MgAl-LDH containing interlayer terephthalate anions. (II) The basic zinc nitrate salt, $Zn_5(OH)_8(NO_3)_2.2H_2O$, consists of infinite brucite-like layers in which 25 % of the octahedral sites are vacant. On either side of the vacant octahedra are located Zn atoms tetrahedrally coordinated by 3 OH^- ions and a water molecule. The nitrate anions located between the layers are not involved in the coordination of the zinc atoms and can be exchanged for other inorganic or organic anions. Here we report the preparation of this material and subsequent exchange of the interlayer nitrate anions for terephthalate anions.

ORIGIN OF SILT- AND CLAY-SIZE PARTICLES IN YOUNG DANISH WIND-BLOWN SAND SOILS

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The silt- and clay-size fractions of about 300 year old wind-blown sand soils in Denmark was investigated. Morphology and general soil analyses show that podzolisation processes have started, but the soils are classified as entisols. In general, the amount of material in the fine fractions increases from the lower to the upper horizons in the soil profiles. XRD analyses of the fine fractions show that the fine-grained material is nearly all quartz and feldspar, though there are indications of the presence of both mica and kaolinite in the most heavily weathered horizons of these young soils. The chemical analyses show a very clear gradient in most of the basic elements from sand over silt to clay. For example, the SiO_2/Al_2O_3 ratio in medium sand is 37, in coarse silt 16 and in clay 5. Thus the elemental analyses highlight mineralogical differences between the particle size fractions, which are not nearly so obvious in the structural data. Though it cannot be excluded that some fine materials originate from atmospheric deposition, the vertical gradient in the content of fine particles, the presence of phyllosilicate mineral particles in the most heavily weathered horizons, and the strong chemical gradients all indicate that most of the material originates from in situ weathering of coarser particles in the soil profiles.

MIXED-LAYER KAOLINITE-SMECTITE IN THE TEPLICE DIATREME, CZECH REPUBLIC

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The Miocene volcanic body close to the Horský thermal spring of Teplice Spa has similar geological form and filling with scoriaceous pipes and chimneys as the Èeské støedohoøí Mts. For explosive basaltoid magma penetrating the anov tectonic zone across the Upper Cretaceous limestones, a relatively rapid, mostly glassy solidification at the top of crater must be assumed. Authigenic volcanic fragments of the volcanic breccia subdivide into: (1) greyish-green, highly weathered olivine-rich basalt containing mixed layer kaolinite-smectite (K/S), (2) vitric basalt, partially altered to dioctahedral smectite)beidellite-montmorillonite series). From the allothigenic fragments mostly crushed clayey limestone, marlstone, silicite, rhyolite, ignimbrite, and metagranite were ascertained. True tuff is rare. Uneven decomposition of the volcanic breccia produced montmorillonitic materials as pseudomorphs after phenocrysts and glassy matrix. In places, minute siderite, dolomite-ankerite and analcite veinlets cross the volcanic fragments. Chalcedony fills some cavities. X-ray diffractograms and microprobe analyses indicate volcanic glass alteration to smectite. Basal reflection 1.508 nm, (ethylene glycol expandion to 1.716 nm)and O6O spacing 0.1497 nm indicate pure dioctahedral smectite. Traces of quartz, siderite, and calcite are identified. The clayey fraction of olivine basalt fragments contain mixed-layer kaolinite-smectite structure, besides discrete kaolinite. The smectite 001 reflection of smectite occurred at 1.499 nm and the O6O- spacing at 0.1497 nm. Ethylene glycol solvation shifted the 001 to 1.716 nm and the 002 reflection appeared at 0.8346 nm. Quantitative estimation, from microprobe analyses shows that the kaolinite-smectite contains 58% smectite and 35% kaolinite. Trace amounts of quartz and goethite are present. Tropical weathering and destabilization by volcanic heating seem to control the alteration of dioctahedral smectite into the interstratified kaolinite-smectite.

ALTERATION OF SODIUM ACTIVATED BENTONITES

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Sodium bentonites have more requested mechanical properties, such as higher plasticity and better viscosity than Ca-bentonites for geotechnical use. Therefore converting Ca-bentonites by adding soda is a commercial process. However, after soda treatment some bentonites lose their preferable mechanical properties and become worthless. Under tropical conditions such alteration process could happen in a few weeks. Three different bentonites were investigated, 2 of them show strong alteration behavior. From each sample the original Ca-bentonite, the soda treated Na-bentonite and the material after experimental alteration were examined. No differences between soda treated and altered samples were determined from the measurements of water adsorption, plasticity and charge density. Mineralogy, exchangeable cations and thermogravimetry data showed slight difference among the samples. Significant changes were observed in microstructure, measurements of nitrogen surface, water take up, helium density and mercury porosity. All findings suggest that microfabric change is responsible for alteration with concomitant decrease in, e.g. viscosity behavior. The following reasons may be responsible for a microstuctural change: calcium/magnesium ratio of exchangeable cation; accessory minerals, new formed carbonates, calcium-silicates and amorphous silicates are potential nucleiifor aggregation and cementation of delaminated clay particles. Further experiments need to be addressed to avoid the changes in microstructure and rheological behavior.

PILLARED CLAYS, DEALUMINIZED ZEOLITES AND ORGANOPHILIC BENTONITES AS ADSORPTIVE ADDITIVES IN CLAY LINERS

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The purpose of clay liners in waste deposits is the protection of the environment by the encapsulation of hazardous compounds. In this respect clay liners are used for both their sealing properties and their significant adsorption capacity. Some contaminants such as heavy metals can be intensively adsorbed often without affecting the soil mechanical properties. Clay barriers show in general a low adsorption capacity against toxic anions and nonpolar organic compounds and in the worst case the liner will lose its sealing properties. In an interdisciplinary research project, funded by the European Union and with partners from the clay producing and applying industry, natural bentonites and zeolites have been optimized with respect to their adsorption properties considering the above mentioned contaminants. The performance of the natural bentonite has been optimized by reaction with either polynuclear inorganic complexes (pillared clays) or organic cationic surfactants (organophilic bentonites). For the natural zeolite an acid treatment has been used. For characterization, standard methods have been used and in addition the adsorption properties have been investigated by batch and percolation cell experiments. Our experiments show, that the optimization process drastically increases the adsorption capacity with respect to the problematic toxic compounds which are hard to adsorb compared to the natural educts. This is due to the fact that the treatment of the dealuminized zeolites and the pillared clays leads to a highly porous surface. The organophilic bentonite offers additional nonpolar adsorption places for the contaminants. In this case the increased adsorption capacity is not caused by a highly porous surface but by network forming organic tails.

INTERCALATION OF AMPHIPHILIC CATIONIC AZOBENZENE DERIVATIVES INTO MONTMORILLONITE AND THE PHOTOCHEMICAL BEHAVIOR

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The intercalation of amphiphilic cationic azobenzene derivatives, p-(w-trimethylammoniopentyloxy)-p'-(dodecyloxy)azobenzene bromide and p-(w-trimethylammoniodecyloxy)-p'-(octyloxy)azobenzene bromide, into montmorillonite have been conducted by a conventional ion exchange reactions. The X-ray diffraction and the elemental analysis results indicated that the most part of the interlayer exchangeable cations were replaced with the azo dye cations. The spectral properties as well as the X-ray diffraction results have revealed that the adsorbed azo dyes aggregate in the interlayer spaces of montmorillonite. Thus, the orientation of the chromophore was controlled by the electrostatic attractions on the negatively charged silicate surface of swelling layered silicates. The intercalation compounds swell in organic solvents and form oriented films by casting the suspensions on substrates. The films were used for the photochemical studies. The intercalated azo dyes exhibit reversible trans-to-cis photoisomerization by UV irradiation and the subsequent visible light irradiation.

STUDY ON HUMIDITY SELF-CONTROL MATERIALS (I):PROPERTIES OF SILICATE MESOSTRUCTURED MATERIALS DERIVED FROM AMORPHOUS FUMED SILICA

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The humidity self-control materials were synthesized using a fumed silica and a quaternary alkylammonium surfactant (decyl-, dodecyl-, tetradecyl- and hexadecyl-trimethylammonium chlorides) as a liquid crystal template under hydrothermal condition. The X-ray diffraction and the transmission electron microscopic observation for heat-treated products indicated to form a homogeneous hexagonal structure of SiO2. The mesostructured products had high B.E.T. surface áreas (ca. 960-1300m2/g) and showed the uniform meso-pore (2-4nm in diameter) structure which was controlled by varying the organic template. As the results of the water vapor adsorption isotherms, the products exhibited the isotherm with sharp increase at the range of relative humidity at 40-60% and the maximum amount of adsorbed water contents of 40-90%.

EFFECTS OF SALT CONCENTRATION ON THE CONSISTENCY LIMITS OF SMECTITIC MARINE CLAYS

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The consistency limits are one of the most important indices of geotechnical characteristics of clays, and the change of saline environment in the depositional and post-depositional processes of marine clays affects their consistency limits. The consistency limits of recent marine clays containing mainly smectite have been measured, using the clay samples saturated with sodium and calcium at different pore water salt concentrations. The results obtained were interpreted in terms of the high or low swelling characters of smectite in the clays. The liquid limit of Na-saturated clays with high-swelling smectite increased with decreasing NaCl concentration, and was greater than the liquid limit of Ca-saturated soil at a 0.01 N salt concentration, which was in accord with the observations for standard bentonite-type smectites. For the clays with low-swelling smectite, however, the influence of salt concentration and cation species on the liquid limit was opposite to that for the high-swelling smectitic clays, being rather similar to that for illite. The low-swelling smectite was found to be a beidellite-nontronite mineral, and the low-swelling characteristics were ascribed to the substitution of Fe2+ for Al3+ in the octahedral layer.

CHARACTERIZATION OF CHEMICAL COMPOSITION OF SPINEL-PHASE IN THE KAOLINITE-MULLITE THERMAL SEQUENCE BY NMR SPECTROSCOPY

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The much-debated chemical composition of the spinel-phase formed during the thermal transformation of kaolin minerals to mullite has been investigated by Si and Al MAS NMR. Kaolinite from Georgia, U.S.A. was decomposed to spinel-phase and amorphous silica by heating at 950C for 24 h, then treated in 4M KOH solution at 90C for 1 h to selectively leach the amorphous silica. This KOH treatment lowered the silica content in the sample from 46.6 to 5.6 wt%. The Si NMR spectrum of the heated sample before leaching showed a single broad peak at -110.3 ppm, assigned to amorphous silica in a three-dimensional framework structure of SiO4 tetrahedra. The leached sample showed resolved Si NMR peaks at -77.5 and -110.2 ppm; the latter is attributed to residual amorphous silica at the grain boundaries of the spinel-phase, whereas the former falls within 2 ppm of the previously calculated position for Si in an Al spinel structure and is therefore assigned to Si incorporated in the spinel-phase. From the relative áreas of the amorphous silica and spinel-phase Si peaks, the amount of SiO2 in the spinel-phase is estimated to be 3.9 wt%. This is the first direct NMR evidence of the incorporation of a small amount of Si in the spinel-phase derived from kaolinite.

SORPTION PROPERTIES OF MESOPOROUS GAMMER-ALUMINA PREPARED BY SELECTIVE LEACHING OF CALCINED KAOLIN MINERALS

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Mesoporous gammer-alumina was synthesized by alkali leaching of calcined kaolin minerals and the sorption properties were investigated. The gammer-alumina samples were prepared by calcining kaolinite from Georgia, U.S.A. at 950C for 24 h and leached by 4M KOH solution at various temperatures for 1 h. The leached samples were washed by deionized water and also by cation exchange resin to remove residue K ions. The porous properties were measured by the BET method using nitrogen and were found to be very narrow pore size distribution at around 3 nm in pore radius. Adsorption-desorption isotherms of water and some kinds of alcohol were measured at 25C. The isotherms of water vapor showed a typical pattern of type IV isotherm and type H1 hysteresis. The adsorption and desorption isotherms showed steep change at high relative vapor pressure region due to capillary condensation from around 0.8 and evaporation from around 0.7, respectively. These relative pressures agreeded well with the calculated ones by Kelvin equation. With elevating the leaching temperature, the specific surface área increased and the adsorption of water vapor increased as well. The maximum amount of adsorption obtained was around 600 ml(STP)/g. The residual K in the samples affected to shift the capillary condensation to lower relative pressure. Sorption properties of alcohols were also examined and compared with those of water vapor.

INFLUENCE OF WATER AND SURFACE HETEROGENEITY ON THE ADSORPTION OF ORGANIC COMPOUNDS ON ILLITES AND KAOLNITES

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Illites and kaolinites are the most active minerals in oil or water adsorption in oil reservoirs. Their relative affinities for oil or water is of great importance in oil recovery and production. In order to compare the behavior of these two types of clays against water or oil adsorption, we studied the adsorption of a mix of organic molecules (models molecules of oil constituents) and water vapor : their interactions with the clays being estimated by inverse gas chromatography (IGC). IGC experiments were performed with different illites and kaolinites of various origins and formation conditions. By IGC at infinite dilution conditions, the dispersive component of the surface energy was determined. A strong decrease, due to the shielding by the water molecules of the sites having the highest energies, is observed. The energetic surface heterogeneity of the clays was examined using IGC at finite concentration conditions, allowing the determination of the adsorption isotherms of organic probes in presence of water. From these isotherms, the adsorption energy distribution functions were computed for propanol-2 and pyridine probes. Water modifies mainly the distribution functions concerning illite whereas practically no change is observed in the case of kaolinite. This observation is certainly related to the higher hydrophilicity of illite in comparison with that of kaolinite and explains the different behaviors of the two families of clay, in oil reservoirs.

EFFECT OF SURFACE ACTIVE SITES ON STRUCTURE FORMATION IN CLAY DISPERSIONS

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One of the main tasks during production of advanced materials from natural clays is purposeful regulation of structure formation. Spatial structures in natural dispersions are spontaneously formed on account of attractive forces and rearrangement is difficult. Our aim was to develop empirical and semiempirical techniques for scientific substantiation of the idea of intermollecular interactions in dispersed clay systems. We used IR-spectroscopy method and ab initio and semiempirical methods of quantum chemistry to research surface and interface of clay minerals. XRD, DTA, adsorption and adiabatic calorimetry techniques were used. Spatial structures and their properties were estimated by rheological methods. Surface electroconductivity method was used to evaluate surface groups effect on physicochemical and structural properties of aqueous clay dispersions. Individual contact's number and strength were calculated based on the model of dispersed porous solid. Natural and monocationic forms of kaolinite were investigated. Experimental results show about (10).13 molecules/m2 on acidic and basic surface active sites (SAS) on clay particles. Their quantity varied during thermal vacuum treatment and depends on the cations substituting etc. SAS change from protonic to aprotic during thermal treatment: dehydration of clay mineral surface about 623 K decreases protonic centre concentration while aprotic concentration increases two times. Comparison of acid-base properties with rheological and physico-mechanical parameters evidenced on their close relationship. Authors suggested the recombination nature of interparticle interactions between clay particles' surfaces with donor-acceptor mechanism of hydrogen bonds formation in case of protonic sites. Aqueous layer elimination during thermotreatment and aprotic site formation leads to H-bonds transformation into covalent chemical bonds and presence of high strength structures.

COLLOIDAL WAYS OF INCREASING CLAY COMPACTNESS

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The regularities of spatial structure formation in semidry powders of compacted clays during compression loading were studied for natural and chemically modified clays of Ukrainian deposits. Physicochemical methods to measure specific surface área, crystallinity, thermal and other properties as well as microscopy were used to evaluate their surface peculiarities. Rheological behaviour was researched during compression. Porosity and structural parameters were measured by the Rebinder technique. Model of porous solid-like body was used to estimate the number and strength of individual interparticle contacts. Brunauer-Emmett-Teller adsorption technique and the method of adsorption from solutions were used to study adsorption properties of compacted clays. Capillary impregnation of compacted samples with a number of liquids was used to compare impregnability. Adiabatic calorimetry method allowed to estimate hydrophilic properties of natural and modified clay minerals surfaces. Colloidal chemical methods to increase compactness of natural clays were developed. Clay surface modification using mineral acid-base treatment showed two pH ranges where the number of individual interparticle contacts and compactness were maximum. Surface treatment with other mineral substances (oxides, salts etc.) gave different results. Surface treatment using organic substances evidenced that the most effective decrease of hydrophilic properties is reached with the help of silicoorganic liquids of low molecular weight. This increases of compactness of clays samples and decreases impregnability with aqueous solutions of mineral and organic substances. In contrast, it favors non-aqueous solution impregnation of compacted clays. The effectiveness of highly compacted clay barriers depends on their hydrophilic properties and composition of impregnating solutions. Compacted clays modified with silicoorganic substances may serve as barriers of aqueous solutions but not non-aqueous ones.

INFRARED SPECTROSCOPIC STUDY OF WATER VAPOR ADSORPTION-DESORPTION BY HOMOIONIC MONTMORILLONITES.

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In recent studies, the hydration and dehydration of homoionic montmorillonites were studied by combining water adsorption-desorption gravimetry, immersion enthalpy measurements, and X-ray diffractograms under controlled water pressure. In order to obtain information at the molecular level about the organization of water molecules, an in-situ infrared study under controlled temperature and water vapor relative pressure was carried out using a special lab-built IR transmission cell. By fitting the infrared spectra, different groups of water can be revealed and their evolution upon hydration and dehydration can be followed. The changes in both the frequency and intensity of the bending vibrations of H2O allows to identify two and sometimes three species of water. In the case of Na-montmorillonite, absorption near 1590 cm-1 can be tentatively assigned to water strongly bound to cations. Two other absorptions bands around 1634 cm-1 and 1664 cm-1 are observed. We propose to assign them to i) water weakly bound to cations and, ii) additional adsorbed water molecules out of the hydration sphere of cations, respectively. Based on the same fitting results, corresponding stretching vibrations of the adsorbed water molecules can be identified as well. The water content also influences the structural stretching vibrations (Al2OH, AlFeOH, and AlMgOH). Comparison between montmorillonites exchanged with different cations confirms the major role of the interlayer cation in organizing the structure of adsorbed water at low water contents.

INFLUENCE OR ORGANIC CONTAMINANTS ON THE COLLOIDAL PROPERTIES OF MONTMORILLONITE DISPERSIONS

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Intensive use of pesticides and other organic contaminats in agriculture and the development of new, ecologically more acceptable pesticide formulations on the basis of clay matrices require knowledge of the influence of organic compounds on colloidal properties of dispersed clay minerals. Principally, addition of salts leads to formation of aggregates. These are flocs at lower particle concentrations and liquid spanning networks at higher particle contents. A study of these reactions provides the basis of understanding the influence of salts and organic substances on the textural structure of soils and on the mobility of fine clay particles in soils. The critical concentration, at which coagulation starts, obeys classical theories of colloid stability only in the case of inorganic salts. Organic salts have a much stronger impact on flocculation due to nonelectrostatic forces. Different cationic and nonionic pesticides, cationic surfactants, and dyes together with sodium and calcium chloride as inorganic reference materials were used in our investigations. The processes of aggregation and disaggregation in concentrated dispersions were measured with rheological techniques. Ion adsorption and coagulation of diluted dispersions were investigated by optical and electrochemical methods. The results are reported in phase diagrams on the colloidal state of the dispersions.

TEM CHARACTERIZATION OF ALIETTITE FROM THE OLYMPUS OPEN-PIT MINE, EASTERN ONTARIO

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Interstratified clay minerals occur in a variety of geologic environments as a result of weathering, diagenesis or hydrothermal alteration, or as a combination of these processes. Aliettite, a regularly interstratified talc/smectite phyllosilicate occurs as a major constituent at the Olympus vermiculite mine, near Stanleyville, Ontario, Canada. The greenish-white, sand- to gravel-size, blocky aggregates developed in altered Precambrian pyroxenites and biotitic paragneisses and are intimately associated with vermiculite, phlogopite, talc, serpentine and diopside. Aliettite was identified by XRD based on its (001) basal reflections of 2.4, 2.78 and 0.949 nm for air-dried, glycerol-saturated and heat-treated oriented mounts, respectively, and an (060) reflection of 0.152 nm. Crushed powder samples supported by holey C film and ultrmicrotomed sections were used for ATEM analyses. Crystallographic work was limited to selected área diffraction due to beam sensitivity, but basal reflections could be related directly to individual crystals using dark field imaging. Aliettite exhibited a smectitic texture but is talc-like in composition (Si:Mg of 2:1; slight trace of Al and Fe), with a measured d-spacing of about 0.9 nm. This rare, Mg-rich, trioctahedral mineral is widely distributed at the site and probably formed as a hydrothermal alteration product of phlogopite and/or talc.

CLAY MINERAL ASSOCIATIONS IN SULPHIDE-BEARING VOLCANICS AND SEDIMENTS FROM THE LIHIR ÁREA, PAPUA NEW GUINEA

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In March-April, 1994, a detailed investigation of the Tabar-Lihir-Tanga-Feni island chain in the New Ireland forearc basin of Papua New Guinea was initiated aboard the R/V Sonne (Cruise SO-94). During the cruise, detailed mapping and sampling of the seafloor and seamounts was undertaken to investigate the tectonics and petrology of this volcanically and hydrothermally active área. Samples were selected from TV grabs, dredges, box and piston cores for whole rock and clay-size mineralogy by XRD on board. This work was followed up by detailed XRD and SEM analysis at the GSC. The suite analyzed included basalts, andesites, pyroclastics and muds with particular emphasis on surface coatings and crusts indicative of hydrothermal alteration, and on sulphides from samples of stockwork-like vein mineralization. The muds contain variable proportions of primary volcanic minerals such as feldspar, pyroxene, magnetite and olivine, as well as carbonates (calcite, aragonite, kutnohorite). Mica, chlorite and smectite occur in minor to trace amounts except in one sulphide-rich sample where Mg-smectite (saponite) dominates. Green coatings, initially thought to be smectitic (e.g., nontronite), were found to be x-ray amorphous. Iron sulphides including pyrite, marcasite, chalcopyrite, galena and sphalerite were detected. Alunite associated with marcasite, Pb sulphate (anglesite?), Pb carbonate (cerrusite?) and halloysite were also observed. In addition, two gold grains were observed through detailed SEM analysis in two different grain mounts from a vug sample. The presence of alunite supports a hydrothermal origin of the observed minerals and is consistent with an acid-sulphate alteration assemblage, typical of subaerial epithermal systems.

THE USE OF SPECTRO-COLORIMETRY TO OPTIMIZE SELECTIVE MINING AND TREATMENT WITH KAOLIN ORES FROM AMAZONAS

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This work aims at a correlation between color and mineralogy of kaolins. The success of usual techniques to improve the kaolins' brightness, depends fundamentally on the nature of the color contaminants (mainly ferriferous and titaniferous minerals). ROM Kaolin samples from the Mina Morro do Felipe, Jari River, Amazon region, were analyzed by spectrocolorimetry of reflectance in the visible range (360 to 780nm), by X-ray diffraction, by X-ray fluorescence, and by EPR. These analyses were also carried out with the following kaolin samples: degritted, centrifuged, treated in a superconducting magnetic separator, and bleached. A correlation between the shape of reflectance spectrum and the presence of contaminants (Fe and Ti) has been studied in order to predict the best beneficiation processes.

DISORDER IN ILLITE: THE DIFFERENCES BETWEEN SHALES, K-BENTONITES, AND SANDSTONES - THE AFM EVIDENCE

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Marked differences between three-dimensional crystal structures of illite and illite-rich illite/smectite (I/S) from fault gouges and shales (FG&S), and K-bentonites and sandstone pore fillings (B&S), have been defined by X-ray diffraction (XRD) studies. FG&S illites are totally disordered by randomly distributed n.60 degree rotations of 2:1 layers about Z*. B&S show well-resolved 11l and 02l peaks indicating 1M structures with minimal rotational stacking disorder. Atomic force microscope (AFM) images of the samples used for XRD also show the two groups are distinctly different. B&S illites typically are plates or laths with planar, nearly featureless surfaces showing a few 10-30 angstrom steps that parallel the fibers. A few laths show stepped terminations suggestive of spiral dislocation growth.

FG&S illites have smaller X-Y dimensions and complex 00l growths showing nucleation and spreading of numerous overlapping 10-30 angstrom thick islands on preexisting surfaces. Some islands have lath-like morphology and are oriented at 0, 120, or 240 degrees to each other. If these growths spread and overlap, a typical 1Md structure would result. The extreme disorder in FG&S illites may result from the presence of small, flat pores, the abundance of detrital mica which acts as a nucleating substrate, and adjacent K-feldspar grains which produce the requisite local supersaturation of K that favors growth by surface nucleation and spreading. Illite growth in B&S may be slow because distal K sources generate low concentration gradients that favor growth by spiral dislocation.

METAMORPHIC COOKEITE IN METAPELITES FROM CAMEROS BASIN (IBERIAN RANGE, SPAIN)

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Cookeite (Li-bearing Al chlorite) is found in metapelites from Cameros Basin, a late-Jurassic - Early Cretaceous Spanish Basin of Northern Iberian Plate filled by homogeneous continental silicic detrital rocks up to 8000 m thickness. This basin (related with a intracontinental rifting) underwent a compressional folding associated to axial plane cleavage coeval with a very low grade metamorphism. This thermal event gave rise, in the deepest part of the basin, to a mineral assemblage of chloritoid, moscovite/paragonite, paragonite, rectorite, chlorite and pyrite. Cookeite occurs in deep áreas as a smooth thin coating of large cubic (up to 25 cm) and pyritohedric (up to 5 cm) poikiloblastic pyrite crystals. Cookeite has also been found in nodules, micronodules and grains. Optical and BSSEM images show that cookeite is commonly an intergrowth with chlorite and minor pyrophillite. Whole rock geochemical pattern, Li contents, REE absolute contents and distributions and Eu anomaly of cookeite bearing rocks, is typical of a shale. Besides, differences on Li contents have not been observed, between cookeite bearing and absent rocks.

Cookeite displays low absolute contents on REE, erratical fractionation and positive Eu anomaly.

On the basis of textural relationships and chemical analysis it has been concluded that the origin of cookeite could be related to metamorphic reactions in a reducing low T- low P environment. The lithium source is likely related to the continental origin of this rocks, being inherited from detrital minerals.

POROUS CLAY HETEROSTRUCTURES

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A new intragallery templating reaction has been developed which greatly expands the use of layered silicate clays and other lamellar compounds for the design of nanoporous solids. By the using appropriate intragallery surfactants as structure - directing agents, intercalates can be synthesized wherein the galleries are occupied by large metal oxide channels, similar to those in mesoporous MCM-41 molecular sieves. The present work describes the templated syntheses of nanoporous silica in the galleries of surfactant - intercalated 2:1 clays, affording what we term porous clay heterostructures (PCHs). Removing the surfactants by calcination affords mesoporous derivatives with surface áreas of 470-750 m2/g and pore widths in the range 14-22 Å, depending on the surfactant system used. These new structures are more stable than large pore molecular sieves because the pore structures are confined between 2D lattices. PCHs provide unique opportunities to improve the properties of surface active lamellar structures by facilitating diffusion of guest species. In addition, owing to the complementary chemical functionalities of the layered and gallery-templated components, PCHs offer new design strategies for heterogeneous catalyst systems.

STRUCTURAL MODEL FOR DEHYDROXYLATED CELADONITES AND GLAUCONITES

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Celadonite and glauconite samples heated at different temperatures were studied by X-ray and electron diffraction. XRD patterns were recorded « in situ » during sample heating as well as after sample heating (« ex situ »). For dioctahedral micas (1 octahedral vacant site per half-unit cell), the in-plane component of the translation between layers (ccosß/a) which is strongly dependant of the position of the vacant octahedral site significantly decreases at temperatures higher than Tmax (temperature of maximum dehydroxylation). Simulation of XRD patterns from different structural models were used to reveal the actual crystal structure of dehydroxylated samples as well as the dynamics of the structural transformations. In non-heated state the samples consist of tv (trans-vacant) 2:1 layers. Initial stage of dehydroxylation is accompanied by the formation of interstratified tv non-dehydroxylated and cv (cis-vacant) dehydroxylated 2:1 layers. After Tmax the dehydroxylated structures consist of cv 2:1 layers in which all originally octahedral cations have 5-fold coordination. The « residual » anions formed after the dehydroxylation reaction occupy the former OH sites with probability equal to 0.5. Migration of cations from cis-sites to trans-sites is accompanied by the transformation of the C-centred layer unit cells into primitive ones, confirmed by SAD. It is found that Al and Mg cations have higher ability to the migrations.

Evidence for cation migration is also deduced from the decreasing of the unit cell parameters during the dehydroxylation process. SAD from dehydroxylated sample provides additional informations concerning the nature of the rotational stacking faults.

SEDIMENTARY FACIES, CLAY MINERAL AND OXYGEN ISOTOPE COMPOSITION OF DEEP MARINE PALYGORSKITE CLAY FROM ODP LEG 159

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During ODP Leg 159 in the eastern Equatorial Atlantic, four sites in water depths ranging from 2 to 4.6kms were investigated including the recovery of drilled core.

In three of the drilled holes, conspicuous blue clays rich in palygorskite with intercalated nodular and irregular concentrations of barite were encountered. Besides palygorskite, the clays contain variable concentrations of smectite, sepiolite, minor quartz, clinoptilolite, opal CT, calcite, and illite. All of these minerals occur in the clay size fraction, but several samples are almost pure palygorskite with minor smectite. Planktonic microfossils indicate an early Eocene age and benthic microfossils are characteristic of deposition well below the shelf edge. Electron microscope observations show that the palygorskite clays consist of a meshwork of delicate Mg-rich silicate fibers. Some fibers were observed to pierce microfossils and are therefore believed to be of a postdepositional origin. The oxygen isotope composition (rel. SMOW) of <2micron separates from clay samples containing variable mixtures of palygorskite and smectite range from 21.5% (palygorskite-rich) to 32.1 % (pure smectite). These values accord with the known range of oxygen isotope values from clays in marine sediments. The petrographic, mineralogic and preliminary stable isotope evidence suggest that the investigated palygorskite formed in situ, at the early Eocene ocean floor. The occurrence of palygorskite in lower Eocene marine sediments is a widespread phenomenon. We attempt to explain its occurrence as a result of the drastic changes in sea water temperature and circulation that characterized the early Eocene oceans.

REE FRACTIONATION TRENDS IN SOME TRANSYLVANIAN GLAUCONIES

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Eight samples of glauconies from the Transylvanian Basin, Romania, representing distinctive stratigraphic levels (within the interval Cretaceous - Miocene), host-rocks and geographic extension of a certain unit, as well as different mineralogical and compositional types were selected and analysed for the REE content, by ICP-MS. All samples show an enrichment in LREE. Sometimes, there is a slight tendency of enrichment in HREE. Two groups of trends can be noticed as far as the total amount of REE resp. the Ce fractionation are concerned. There is a group of samples geographically related to the north-western área of the Transylvanian Basin, in which the total REE content is higher as compared to the other samples; also Ce is evidencing a slight positive anomaly. The other group, mainly representing the south-western áreas of the Transylvanian Basin, shows lower total REE contents and generally, Ce is relatively depleted. A quantitative interpretation of the REE patterns took into account the total REE content, the Ce anomalies, the controls of the bulk chemistry, the substrate, the host-rock, sea-water and that of stratigraphic ages on the REE pattern, as well as the regional overprint on the REE fractionation trends. The quantitative parameters which yielded interesting aspects on the REE patterns in Transylvanian glauconies are: Ce and Eu anomalies (Ce n/Ce n, Eu n/Eu* n), the total REE content, LA/Ce, La/Ce, La/Nd, as well as La n/Yb n, Yb n/Nd n and Er n/Nd n ratios. In conclusion, the ancient glauconies seem to display more differentiated trends in the REE pattern, than it was previously mentioned.*

DETERMINATION OF MINERAL COMPONENTS COMPRISING SERPENTINE DEPOSITS IN CALIFORNIA

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Mining operations in serpentine quarries requires an investigation for possible fibrous chrysotile. Powder X-ray diffraction experiments show a linear relation between the peak height of the (111) reflection and the amount of 1T lizardite. There is also a linear relation with the spacing of the second order basal spacing, ranging from 0.3619 nm and 0.3649 nm. The determination of the amount of lizardite and clinochrysotile present is then adjusted for any orthochrysotile. All of the 26 different serpentine deposits investigated are more than half chrysotile, and antigorite occurs separately. The amount of the rare 6T lizardite, basal spacing 0.3637 nm, and lizardite in dunite, at 0.3602 nm, can be estimated by the (11.6) and (111) peak heights only. The formation of chrysotile macrofibers is restricted by the presence of FeO in excess of about 3% in the crystal structure. The fibrous chrysotile tested ranged from 0.9% to 2.7% FeO, and lizardite-chrysotile specimens ranged from 2.4% to 9.4% FeO, NiO ranged from 0.13% to 0.58%, and both MnO and Cr_2O_3 present. The main associative minerals are chlorite and hematite.

ORDOVICIAN K-BENTONITES IN THE ARGENTINE PRECORDILLERA: ORIGIN, COMPOSITION, DIAGENESIS, AND PALEOENVIRONMENTAL IMPLICATIONS

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Middle Ordovician K-bentonites from Cerro Viejo and Talacasto in San Juan Province, Argentina, representing altered vitric rhyolitic fallout ash are being studied due to their multiple potential for diagenetic, stratigraphic, and paleogeographic interpretation. Zircon U-Pb dating reveals a lower concordia intercept age of 463±2 Ma (Llanvirn) and an upper intercept age for inheritance uranium of 1234 Ma (Grenville). These record both the time of volcanism and the age of the parental magma source rock. The clay minerals are mainly illite-smectite and illite-chlorite mixed layers with R values between R1-R3. Trace and major element analysis of both bulk rock and selected phenocrysts by ICP and EMP reveal a selective enrichment of elements of low ionic potential (Sr, K, Rb, Ba) and low abundance of elements of high ionic potential (Ta, Nb, Ce, P, Zr, Hf). This indicates that the K-bentonites were associated with felsic explosive volcanism of island-arc or collision plate margin type probably during the docking of the Precordillera terrain with Gondwana. The distribution of Conodont Alteration Index values (up to 3) in the outcrop áreas indicates that the maximum burial temperatures for this region did not exceed 150-200 C. That allows us to assume that the clay minerals have retained the isotopic composition acquired during their formation in a shallow to intermediate water depth marine environment. Oxygen isotope fractionation equations of Sheppard and Gilg,1996, will be used for estimation of paleotemperatures of clay mineral formation.

1.1.1.1.1. Anexos Edafología

CLAY MINERAL "ANOMALIES" IN SURFACE Ah HORIZONS REVEALED BY FINE-INCREMENT SOIL SAMPLING

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Several soil profiles were sampled in 1 cm increments throughout the Ah horizons to measure the rates of soil faunal activities. The distribution with depth of bomb fallout ^{137}Cs within the Ah horizon was measured to infer the influence of earthworms during the last 50 years. In soil profiles where the earthworm L. terrestris *casts at the soil surface, the most weathered clay minerals in the Ah horizon occurred in sample increments below the surface layer. The degree of clay mineral weathering is determined by measuring the área under the 1.4 and 1.0 nm peaks, and the área of interstratified minerals between these peaks. The áreas were measured using Jandel® Peakfit software. In a soil without surface-casting earthworms the most weathered clay minerals occurred in the surface 1 cm layer. The sampling methods for short-term (< 100 years) soil genesis studies are discussed. The implications of the findings to pedogenic clay mineral weathering studies are also discussed.*

Containment and Stabilization of Buried Waste

Task Description

This technology will develop, demonstrate, and implement advanced grouting materials for in situ stabilization of contaminated soils and the placement of impermeable, highly durable subsurface barriers. The effort focuses on cementitious and soil cement mixtures compatible with commercially available placement techniques. The developed super-plasticized grouts and soil cements have significantly superior mechanical, physical, and durability properties than those of conventional formulations. The permeabilities are two to five orders of magnitude less than for other materials frequently used as caps and barriers such as clay, soil-bentonite, and cement bentonite slurries. Therefore, the dimensions of the barriers can be reduced significantly. When used for stabilization, blast furnace slag modified grouts—soil mixtures placed by jet grouting or soil mixing—can stabilize and solidify soils contaminated with trivalent or hexavalent chromium in a one stage process. The treated soils pass the EPA Toxicity Characteristic Leaching Procedure. They also have high strength, low permeability, and resistance to wet-dry cycles.

Benefits The benefits from this work include: 1) reduction in costs compared to those of excavation, treatment, and disposal, 2) improved operations, thereby increasing regulatory agency and public acceptance, and 3) reduction of health and environmental risks as compared to those from the use of other remedial techniques.

Collaboration/Technology TransferIndustrial interest in the technology has been expressed by major world-wide geotechnical construction firms.

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1.1.1.1.2. Anexos Química

THE STRUCTURE OF INTERCALATED KAOLINITES: A RAMAN AND INFRARED SPECTROSCOPIC STUDY

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Changes in the molecular structure of highly ordered kaolinites, intercalated with urea, potassium acetate and caesium acetate have been studied using vibrational spectroscopy. A new Raman band, attributed to the inner surface hydroxyl groups strongly hydrogen bound to the acetate, is observed at ~3605 cm-1 for the potassium and caesium acetate intercalates with the consequential loss of intensity in the bands at 3652, 3670, 3684 and 3693 cm-1. Remarkable changes in intensity of the Raman spectral bands of the lattice region of the kaolinite occurred upon intercalation. In particular, the 144 and 935 cm-1 bands increased by an order of magnitude and were found to be polarised. These spectroscopic changes provide evidence for the inner surface hydroxyl group-acetate bond being at an angle approaching 90 to the 001 face. Decreases in intensity of the bands at 243, 271 and 336 cm-1 were observed. The urea intercalate shows new Raman bands at 3387, 3408 and 3500 cm-1 and are attributed to new N-H vibrations upon formation of the urea-Si2O5 complex. Pronounced changes in the structure of the delaminating molecules were also observed. DRIFT results are complementary to the Raman microscopic investigations and have proven particularly useful in the study of the hydration sphere of the intercalating cation and the possible effect of the cation on the position of the band assigned to the inner hydroxyl group.Differences in the dehydroxylation mechanisms of highly ordered kaolinites intercalated with potassium acetate, caesium acetate and urea were studied using simultaneous TG-DTG-DTA and TG-MS methods.

INTERACTION OF STRYCHNINE WITH KAOLINITE AND MONTMORILLONITE : A RAMAN SPECTROSCOPIC STUDY

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The pesticide strychnine, an alkaloid with heterocyclic structure, is used extensively throughout the world for pest animal control. The Raman spectra of strychnine adsorbed on both kaolinite and montmorillonite showed spectral changes indicating chemical interactions. The strychnine-kaolinite complex showed several changes in the Raman microprobe spectra: the peak at 2895 cm-1 shifted to higher wavenumber with an additional band at 2837 cm-1. The bands at 1662 and 1595 cm-1 shifted to 1599 and 1666 cm-1. A number of changes occurred in the region below 1000 cm-1including changes in peak intensity, the lack of intensity of peaks at 570, 450 and 226 cm-1 and the appearance of an additional peak at 476 cm-1. Such spectroscopic changes show significant interactions between the tertiary amidegroup and the kaolinite. The strychnine-montmorillonite complex also showed several changes in the Raman spectra. This included a peak shift from 3044 to 3048cm-1 and the overlapping doublet at 3072 cm-1 separating into smaller peaks at 3060 and 3058 cm-1. The peak at 3097 cm-1 shifted to 3103 cm-1, and additional peaks at 3193 and 3110 cm-1. The bands at 1662 and 1595 cm-1 shifted to 1666 and 1614 cm-1. As with kaolinite, there is evidence for interactions between the tertiary amide group and the montmorillonite. Most of the changes occurred in the strychnine bands. Formation of positive charges on the amine groups, hydrogen bonding and van der Waals forces account for surface interactions between the strychnine and the clays.

ALTERATION PRODUCTS OF EXPERIMENTALLY WEATHERED BIOTITE: A HIGH RESOLUTION TEM (HRTEM) AND MÖSSBAUER SPECTROSCOPY (MS) STUDY

E. A. Ferrow, Lund University, Lund, Sweden

MS is a bulk technique and provides averaged information on the chemical state of Fe, while HRTEM has atomic resolution and provides structural information on solid state reaction mechanisms. In this paper we will discuss the weaknesses and strengths of the two techniques and present the potential of combining them using experimental weathering of bioitite as an example.To this end a natural biotite sample was reacted in HCl and H2SO4 solutions at different pH. The reaction products were removed by a continuous flow of an external eluent that was in contact with the mineral suspension through a dialysis membrane. ME and HRTEM show that the main factors that determines the degree of oxidation are the pH of the solution and the K selectivity of the solid phase. During oxidative weathering charge *neutrality is maintained primarily by octahedral cation ejection; while tetrahedral cation ejection and deprotonation prevail at low pH and high pH, respectively. Thus weathering is controlled primarily by pH and by the oxidant used. Once equilibrium has been reached, then, further weathering does not affect the oxidation state of iron. TEM and SAED show that both weathering and layer expansion by alkalyammonium ions are discontinuous processes. There is a certain 'critical' concentration of Fe and K in solution over which further weathering and layer expansion are blocked resulting in a quasi periodic texture. Moreover, TEM shows that the tetrahedral layer collapses during the last phase of weathering leaving an amorphous phase rich in Si, Al and Fe.*

DYE-SURFACTANT COMPETITIVE ADSORPTION ON CLAY PARTICLES IN AQUEOUS SUSPENSION

J. A. Ferreira and F. Gessner, Universidade de São Paulo, São Carlos, SP-Brasil

The exchangeable cations present on montmorillonites can be replaced by long-chain quaternary ammonium cations, the resulting clays having some useful properties, e.g., they are able to swell and to disperse in a variety of organic solvents, having a wide range of industrial applications. In order to understand better the processes that govern the adsorption of these compounds on the clay surfaces, we studied the competitive adsorption of a cationic dye (methylene blue) and surfactants (quaternary ammonium salts having different chain lengths) on SWy-1 montmorillonite. The methodology used is based on the changes in the absorption spectrum of the adsorbed dye, and significant changes were detected observing the time evolution spectra of the dye-clay-surfactant system. These changes were associated to different processes occurring in these systems. Increasing the surfactant concentration, an increase in the dye aggregation on the clay surface is observed, followed by a slower migration of dye molecules to the internal domains of the clay particles. Moreover, the process in the clay-surfactant-dye systems involves mainly 'particle-particle' interactions, and consequently the displacement of the dye molecules on the surface of the clay particles is inhibited. It is important to note that the adsorption of the dye and the surfactant molecules occur initially mainly on the external surfaces of the clay particles. As time passes, migration of surfactant molecules to the internal region of the particles also occurs, competing with the dye molecules for the sites in this region. These processes are also sensitive to the chain length of the surfactant molecules.

CHANGES IN D-SPACING AND ORGANIZATION OF A Na AND Ca SMECTITE DURING EMBEDDING PROCEDURE AND TEM OBSERVATIONS

F. Elsass, A. Beaumont, A. M. Jaunet, M. Pernes and D. Tessier, INRA, Science du sol, Versailles, France

Clay pastes of Na- and Ca-Wyoming montmorillonite were prepared at low suction pressures and examined at different stages of the embedding procedure using XRD for determining layer distance and particle orientation. Sample preparation for TEM analysis followed the method of Tessier (1984). The wet clay samples were first immersed in pure methanol, then propylene oxide, and finally Spurr resin.The polymerization was made at 60°C for 24 h. At 3.2 kPa as well as at 1.0MPa, the clays exhibit layer distances of 19.0 Å for Ca and Na. After methanol exchange, the layer distance collapsed to ~16 Å. With other solvents, the samplesbehaved in a similar way to that of methanol. The same behavior was observed with the components of the resin, even after polymerization. Another drop was observed in the column of the microscope since the layer distance was 14 Å, both for Na and Ca. Examining the particle orientation demonstrated that after solvent exchanges the microstructure remained similar to that of the clays in water. It is concluded that the organization of the smectite is preserved. The TEM observations confirmed that the embedding procedure preserves both orientation and texture (number of layers) of the clay. Nevertheless, the layer distance depends on the nature of the solvents, including the components of the resin, their behavior under vacuum, and finally the clay properties (layer charge and location).

CHEMICAL EVOLUTION OF CLAYEY BACKFILL MATERIAL DURING INTERACTION WITH NUCLEAR GLASS UNDER THERMAL GRADIENT

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Several reference concepts for deep geological HLW disposal include a clay engineered barrier (EB), a steel canister and a glass waste form. Consequently, the interactions between glass dissolution, steel corrosion and clay

mineralogical evolution are important to consider for the assessment of the long term confinement capability. The initial thermal gradient (expected duration 1000 years after closure) is an additional driving force for the migration of elements from the glass. Experimental systems with higher gradients than expected in the future repository are useful to enhance transport and interaction mechanisms, provided that these mechanisms are transferable to real conditions. We developed experiments under thermal gradients in which a simulated nuclear glass interacted with backfill materials with various Si/Al ratio (1.5, smectite; 1, kaolinite; 0.6 allophane). Experiments were conducted in closed gold tube disposed in cold-seal vessels at 140 bars during 100 days and submitted to a thermal field 300-200°C. Newly formed products were studied by means of integrated in-situ analyses using SEM and TEM observations, XRD identification and EDS analyses. Comparison between the experiments performed with backfill material with different Si/Al ratio allowed us to determine (i) a systematic recrystallisation of the clayey material whatever the initial Si/Al ratio; (ii) a migration of major elements such as Si, Al, B and alkali elements through the clayey material; (iii) an efficient chemical trapping of the heaviest elements (Fe, Zn, Zr) at the glass / clay interface. Such results have important consequences for HLW disposal concerning long-term evolution and migration properties of EB.

FAR INFRARED STUDY OF CATIONS LOCATED IN THE HEXAGONAL HOLES AND THE OCTAHEDRAL CAVITIES OF PHYLLOSILICATES

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Cations (M) located in the hexagonal holes (Mc) and the octahedral cavities (Mo) of phyllosilicates give absorption bands in the far infrared (FIR) range. FIR spectra are recorded with a BRUKER IFS 113V. To identify and to characterize the FIR bands of compensating cations (Mc) spectra of phyllosilicates which have no Mc(pyrophyllite, talc) were compared with spectra of phyllosilicates which have K in their interlamellar spaces (muscovite, phlogopite, biotite) or with weathered micas and vermiculite saturated with monovalent or bivalent cations. In-plane and out-of-plane dichroïc experiments show that there are three modes of vibration for Mc.One~140 cm-1 is parallel to the c axis and two~90 cm-1 are parallel to the a and b axis. To identify and to characterize Mo FIR bands, phlogopites were synthesized with increasing amounts of Fe++, Co++ and Ni++ substituted to Mg++. Shifts of absorption bands are observed which make the assignment of bands~160 cm-1 to Mo possible. Other FIR experiments were performed with phlogopites synthesized with different OH/F ratios. The FIR band shifts are a function of : (1) (Z/µ)1/2, where Z is the charge of the cation and µ the reduced mass of the oscillator M-Oxygen, (2) the respective size of the cation and of the cavity, (3) the structure (tetrahedra rotation angle), (4) the chemical composition of the sheets (Fe++/Fe+++ratio, etc.), (5) the fluorine content. So, the use of compensating and octahedral cations as spectroscopic probes to get more information on their state and location but also on their local environment is discussed.

APPLICATION OF CS-AND SR-ABSORBING PROPERTIES OF THE BLUE CAMBRIAN CLAY IN SOLVING ENVIRONMENTAL PROBLEMS

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Clay minerals, especially smectite and mixed-layered minerals, are capable of ion exchange and absorbing of organic and inorganic components from solutions. We studied these properties for the <0.005-mm fraction of a blue Cambrian clay, widely distributed to the south of St.Petersburg. The clay comprises dioctahedral illite-2M1, chlorite and quartz. Absorbing capacity of the blue clay with respect to Cs and Sr was determined. 600-mg samples of the clay were kept in 0.001M,

0.01M and 0.1M-solutions (6cm3) of CsCl and Sr(NO3)2 for 1 hour to 3 days at 20C. To reveal effects of mineralized waters and acid rains on the clay saturated in Cs and Sr, the latter was treated with 0.1M-solution of NaCl and 0.1%-solution of HCl for 24 hour. Absorbing capacity of the clay was determined by X-ray fluorescence. The clay intensively absorbs Cs and Sr within the first hour and increased exposure has no further effect. At low Cs and Sr concentrations (0.001M),

the clay absorbs 68% of these cations. At higher Cs and Sr concentrations (0.01M and 0.1M) the absorption decreases: Cs-7.5%, Sr-29% and Cs-0.75%, Sr-3.42%, respectively. The higher Cs and Sr concentrations in the solution, the higher are their contents in the clay sample. The Cs-and Sr-saturated clay treated with 0.1M NaCl loses 61% Cs and 67% Sr.The clay treated with 0.1% HCl loses 66% Cs and 99% Sr. For solutions containing radioactive Cs and Sr, the activity of CsCl solution decreases 5% within 1 hour and 9% within 3 days, and the activity of Sr decreases in 3.7% and 4.2%, correspondingly. The blue Cambrian clay can be used as an absorber of radioactive nuclides such as Cs and Sr, which contaminate the environment.

PHASE ANALYSIS OF CLAYS BY EXPERT SYSTEM

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Clays are major components of soils and sediments. They generally consist in a mixture of a) phyllosilicates with a periodic structure, b) mixed-layer phyllosilicates and c) associated minerals. Mixed-layer minerals themselves differ in the type of layers they contain and in the way these layers stack, yielding an infinite variety of possible X-Ray diffraction patterns. An additionnal complication in the interpretation of the XRD pattern is caused by the mixture. We propose here an expert system for the phase analysis of clays. It requires the oriented sample XRD patterns for three states of the sample: air-dried, saturated with ethylene-glycol, heated at 500°C. The expert system is built into five independant parts. The first one identifies the associated minerals. The second determines the occurrence of pure (periodic) phyllosilicates. The third one identifies the nature of the mixed-layer minerals present in the sample (i.e. the types of the layers they contain); it is mainly based on the evolution of the patterns after glycolation and/or heating. The fourth one proposes for a given mixed-layer mineral its structural characteristics (i.e. the abundances of layers and the reichweite); it is mainly based on rules like the Mering's one or diagrams as the Watanabe's one. The fifth part provides a calculation tool of X-Ray patterns which uses as input data the informations provided by the parts 3 and 4, and allows a refinement of the structural parameters of mixed-layer minerals. This program runs on Windows95 PC-compatible computers.

1.1.1.1.3. The use of soil blocks, timber poles and micro-concrete roofing tiles for house construction in Sri Lanka

The problem

Large section of the population in the urban and rural áreas of Sri Lanka have inadequate housing conditions, since most housing is unaffordable for the low-income groups. The cost of housing could be reduced if families would be more actively involved in the construction of the houses using locally available building materials.

The projects

Thanks to the projects, more than 150 families living in poor conditions were able to build good permanent houses. The first housing project was the semi-urban Puwakpitiya project: 27 houses were completed between June 1993 and May 1994. The second project was the rural Kosgama housing project: 20 houses were completed between October 1994 and March 1995. A further 62 houses were completed in Madegama and Paliyutu and several large housing projects (one in the east of Sri Lanka with 500 houses and one in the Hill country with 250 houses, passed the preliminary planning stage and construction started before the end of 1995. The latest on-going semi-urban project is in Kajughalanda, a village just outside Colombo's municipal boundaries and consisting of 90 houses. The site is used for training technical officers of the National Housing Development Authority (NHDA).

The approach

The approach aims at maximizing the contribution and participation of the users, i.e. the poor people, at maximizing the use of building materials available at the building site and the locality, and at minimizing the damage to the living environment. To achieve this, the beneficiaries manufacture cement-stabilized compressed or interlocking soil blocks using soil available at the site; boron-treated small diameter timber poles are used for the roof structure; micro-concrete roofing (MCR) tiles are used to replace conventional asbestos sheets, clay tiles or corrugated iron sheets. The small-scale enterprise which manufactures the MCR tiles creates a few jobs, mainly for women.

The new materials and technology have to satisfy the requirements of current building specification, building standards and other requirements of the local authorities. It was decided that for urban housing the new soil-cement blocks should have the same strength and durability as sand-cement blocks. Therefore, 5 per cent cement-stabilized interlocking blocks were used in the Kajughalanda urban housing project.

There are no enforced building regulations or building specifications for the construction of houses for the poor in the rural áreas of Sri Lanka and it was not considered relevant to apply specifications used for middle-class housing in housing for the poor. Therefore, it was decided that the soil-cement blocks should have the same strength as other building materials currently used by the rural poor. Because the normally available sand-cement blocks have a strength of around 0.6 N/sq.mm., 3 per cent stabilized soil blocks were used for the construction of houses in the rural áreas.

The durability of the small-diameter timer poles was assured by chemical treatment of the timber and the strength of the timber poles was established by conducting tests for bending stress, shear stress and creep stress at the University of Moratuwa. Based on the results of the strength and the creep tests, a roof design was made. For the micro-concrete roofing tiles, the Institute for Construction Industry and Development provided the strength and quality control methods.

The NHDA had to change some of its institutional arrangements, management system and decision- making process to introduce the new technologies and to achieve maximum user participation. In normal housing projects, the NHDA employs contractors to construct the houses or provides financing and technical assistance to individual home builders. In these projects, the NHDA collaborates with LEADS, a non-governmental organization which is familiar with the technology and has experience with building houses using this technology and community participation. The Kajughalanda housing project had a management system which involved LEADS, a community organization as well as local politicians.

A few problems were encountered with the introduction of the new technologies. The main technical problem faced in self-help projects is the proper manufacturing of the soil-cement blocks, include the control of moisture, over- and under-pressing of the blocks and proper curing. Over-pressing often leads to machine breakdowns. Achieving the correct slope of the roof and level roof were the main problems with respect to the micro-concrete roofing tiles. No significant problems were encountered when the small-diameter poles were introduced. Although in all projects the problems were not fully overcome, most problems can be solved satisfactorily by conducting training to home builders and project officers.

The impact

The use of soil blocks, treated timber poles and MCR tiles makes it possible to produce a house which is 50-70 per cent cheaper than the same house with the next cheapest traditional building materials such as burnt bricks, clay tiles and coconut timber rafters. The use of soil blocks and MCR tiles reduce the energy use (in the form of fire wood) by more than 40 per cent. Small diameter timber poles are a by-product of plantation forest thinning and are usually left in the forest to decay. They can be used for the roofs as a substitute for clay tiles and asbestos roofing sheets. The only factory- produced materials are cement (40 bags of 50 kgs each per house), 12 kgs of boron chemicals and small items such as nails, hinges etc.

Cost breakdown of houses

	Rural	**Urban**
Skilled labour	17.86%	17.78%
Self-help labour	28.57%	26.67%
Factory materials	35.71%	22.22%
Local materials	17.86%	33.33%
Total	100.00%	100.00%

Since more than 80 per cent of the materials is locally available, the approach has a good potential for broader application and has a good sustainability. More than 70 per cent of the soils in Sri Lanka is suitable for soil-cement blocks; more than one million poles are cut at plantation forest thinning and are left to decay each year and good river sand is widely available.

The direct cost of materials and skilled labour was Rs.24,000 (US$480) for a rural house of 350 sq.ft. (33 sq.m.) and Rs.45,000 (US$900) for an urban house of 350 sq.ft. The total value of the unskilled labour provided by the users can be estimated at Rs.8,000 or 20 per cent of the total value of the house. These costs are quite compatible with government grants or loans to low-income groups which amount to Rs.15,000. Note that a house costing less than Rs.50,000 is within the means of a low- income family whose income is around Rs.1,500 per month and that a house built with traditional building materials costs about Rs.75,000.

Acceptance of the building materials by the users, professionals and human settlements organizations was measured through a structured questionnaire and opinion surveys. The surveys recorded varying degrees of user acceptance during the project cycle. There usually was a high level of acceptance at the start of the project (80 per cent); a drop in acceptance in the early stages of construction (45 per cent); and a good level of acceptance towards the end of the project (70 per cent). The drop in acceptance in the early phase of construction occurred when the beneficiaries had to produce the blocks and a few technical problems arose and when some participants were too lazy to produce blocks or carry out other work.

The professionals and organizations showed a very low level of acceptance in the early stages of the project. However, the successful completion of the second project (in Kosgama) had a major impact on the level of acceptance by the professionals and the human settlements organizations. The improvement of the technology (e.g. the introduction of the interlocking soil blocks) also helped to increase the acceptance of the materials by the beneficiaries and the professionals. The Kajughalanda housing project demonstrated the positive impact of good partnership between the village development committee, a government organization (NHDA), a non-governmental organization (LEADS) and an academic institution (the University of Moratuwa). The NHDA acted as the promotor of the project and the supplier of building materials; it also conducted the training for technical staff. The NGO acted as the implementing agency; the University provided the required technology and technical information and did the necessary teaching.

Reference:

Submission to the Best Practices Initiative of the Habitat II Conference

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1.2. Cursos

Projet "TERRA" Project *- PAT 99 - Conservación y Manejo del Patrimonio Arquitectónico Histórico - Arqueológico de Tierra*

Fechas: *31 Octubre - 10 Diciembre 1999*
Sitio: *Chan Chan, Trujillo, Peru*
Idioma: *Español*

Antecedentes: *El Segundo Curso Panamericano sobre la Conservación y el Manejo del Patrimonio Arquitectónico Histórico-Arqueológico de Tierra forma parte del desarrollo del* Programa Integral para la Conservación del Patrimonio Monumental de Tierra *del Instituto Nacional de Cultura La Libertad (INC-LL). Con tal iniciativa el INC-LL se propone promover, en el largo plazo, actividades integradas de formación, investigación, documentación, cooperación y sensibilización en materia del estudio, la conservación y el manejo del patrimonio arquitectónico histórico-arqueológico construido con tierra. En el marco de tal programa, el INC-LL organiza un segundo ciclo de formación profesional especializada en acuerdo de cooperación con el Centro Internacional para la Construcción de Tierra - Escuela de Arquitectura de Grenoble (CRATerre-EAG), el Centro Internacional de Estudios sobre la Conservación y la Restauración de Bienes Culturales (ICCROM), el Instituto Getty de Conservación con contribuciones de: el Fondo del Patrimonio Mundial de la Unesco, la Organización de Estados Americanos la (Comisión de Comunidades Europeas: Dirección General 1B, Relaciones Exteriores del Mediterráneo del Sur, el Medio y Cercano Oriente, la América Latina, el Asia de Sur y del Sudeste y la Cooperación Norte-Sur), la Oficina de Representación de la UNESCO en Perú, el Ministerio Francés de Asuntos Extranjeros y la Embajada de Francia en el Perú, la Municipalidad Provincial de Trujillo, el Consejo Nacional de Ciencia y Tecnología del Perú y numerosos entes internacionales y nacionales públicos y privados.*

Descripción: *El curso consiste en un ciclo intensivo de seis semanas de formación profesional especializada "in-situ" en la Zona Arqueológica de Chan Chan, la Ciudad de Trujillo y otros sitios del patrimonio arquitectónico histórico-arqueológico de los Valles de Moche y Chicama en la Región de La Libertad, Perú.*

El curso se estructura alrededor de un conjunto de asignaturas que promueve un enfoque interdisciplinario entre las diferentes categorías de los participantes al ciclo de formación. Del plan común se derivarán actividades académicas en áreas especializadas que se desarrollarán a través de lecciones teóricas, demostraciones, ejercicios de laboratorio y práctica de campo, tareas, presentaciones de casos de estudio y de problemas específicos, visitas, discusiones, informes y otras actividades afines. El desarrollo de tales actividades requerirá la plena participación de los asistentes al curso durante todo el período del ciclo de formación intensiva.

En el marco de la planificación de la conservación y del manejo del patrimonio histórico-arqueológico, el curso pondrá particular atención en las características específicas del conocimiento científico existente en el campo del patrimonio arquitectónico construido con tierra, incluyendo aspectos relacionados al problema de las superficies arquitectónicas decoradas, pinturas murales y relieves polícromos en soportes de tierra, el riesgo y patologías sísmicas y el control continuado, en el marco del desarrollo de planes de conservación y de manejo de tal patrimonio.

Asignaturas: *El sílabo del curso incluye las siguientes materias*
historia y universalidad de la arquitectura de tierra;
el patrimonio arquitectónico histórico-arqueológico americano construido con tierra;
superficies arquitectónicas decoradas, pinturas, murales y relieves polícromos en soportes de tierra;
historia, teoría, filosofía, principios y criterios de conservación;
la planificación de la conservación y del manejo;

métodos y técnicas de facilitación/moderación de la participación en el proceso de planificación;
la documentación;
la formación, identificación y caracterización de la tierra como material de construcción;
tecnologías de la construcción con tierra;
patologías de la construcción de tierra; estructuras, superficies, humedades, sismos;
prospección y evaluación de condición y del contexto;
desarrollo de estrategias de conservación y de manejo;
técnicas de conservación de estructuras;
problemas de conservación de pinturas murales y relieves polícromos en soportes de tierra;
técnicas de manejo de sitios histórico-arqueológicos;
el control continuado.

Sede: *El curso se impartirá en la sede del Museo de Sitio de Chan Chan (Zona arqueológica inscrita en 1986 en la Lista del Patrimonio Mundial en el cuadro de la Convención sobre la Protección del Patrimonio Mundial y Natural de la UNESCO). El curso desarrollará actividades conexas en el Teatrín del INC-La Libertad y en el Auditorio de la Casa del Mariscal De Orbegoso (Monumento Histórico de la Ciudad de Trujillo)*

Alcances: *El curso tiene el objetivo de promover*
un enfoque científico, metodológico e interdisciplinario hacia el estudio, la conservación y el manejo del patrimonio histórico-arqueológico construido con tierra;
el desarrollo y la ejecución de planes de conservación y de manejo adecuados a las características específicas de tal patrimonio;
la comunicación y participación de las disciplinas responsables del estudio, la conservación y el manejo de tales sitios;
la sensibilización profesional e institucional en materia del estudio, la conservación y el manejo del patrimonio arquitectónico histórico-arqueológico construido con tierra;
el desarrollo de programas universitarios en el tema;
la formación de formadores;
el desarrollo de acciones contínuas hacia la conservación y el manejo del patrimonio arquitectónico histórico-arqueológico de tierra en la región.

Participantes: *El curso se dirige a profesionales en antropología, arqueología, arquitectura, ingeniería, conservación u otras disciplinas vinculadas a la conservación del patrimonio, técnicos y/o personal con al menos tres años de experiencia en la conservación y/o el manejo de sitios históricos-arqueológicos construidos con tierra. Los postulantes al curso deberán demostrar actividad en el marco de los programas de instituciones culturales o universidades de las Américas con iniciativas en el campo de la materia del curso.*
Los participantes serán seleccionados en base a sus antecedentes de formación, experiencia profesional y actividad en relación a la conservación y/o el manejo del patrimonio arquitectónico histórico-arqueológico de tierra. El número de participantes será limitado a 25/30 personas.

Matrícula y Viáticos: *El costo de la matrícula en el curso es de US$ 2300.00 dólares; cuota que incluye el costo de la inscripción, del material didáctico, del alojamiento y de las comidas en la Ciudad de Trujillo durante los 41 días del período comprendido entre el 31 de Octubre y el 10 de Diciembre de 1999 incluso; además de los costos de transporte organizado desde la Ciudad de Trujillo a la sede del curso en el Museo de Sitio de Chan Chan, a visitas y trabajos de campo. Cada participante será responsable de los gastos del viaje de ida y vuelta desde el lugar de origen a la Ciudad de Trujillo, Perú.*

Información: *Para obtener detalles en relación al sílabo, las solicitudes y formularios de admisión, la selección de participantes y las matrículas, sírvase escribir, indicando sus datos y dirección postal, a cualquiera de las siguientes institucionesPAT99ICCROMVia di San Michele 13I-00153 ROMA RMItalia PAT99CRATerre-EAG (Formation)BP 263660 avenue de ConstantineF-38036 GRENOBLE Cedex 2 France*

PAT99The Getty Conservation Institute (GCI)1200 Getty Center Drive, Suite 700LOS ANGELES, CA 90049-1684USA **PAT99**
Instituto Nacional de Cultura - La Libertad (INC-LL) Independencia 572 TRUJILLOPeru.

TIERRA: CONSTRUCCIÓN Y RESTAURACIÓN
ETS Arquitectura de Valladolid - Amayuelas de Abajo (Palencia)
Del 25 al 27 de Mayo de 2001

VIERNES-25 SALÓN DE ACTOS ETS Arquitectura de Valladolid
17,00 - Presentación de las Jornadas. Juana Font Arellano, Licenciada en Arte.
17,15 - Ponencia - El valor de mantener el patrimonio construido,
José Jiménez Lozano, escritor.
18,00 - Ponencia - La Tierra como material de construcción,
Enzo Siviero, Ingeniero. Escuela de Arquitectura de Venecia, Italia.
19,00 – Ponencia – Restauración de Tapial Soluciones prácticas.
Hubert Guillaud, arquitecto. CRATERRE, Grenoble, Francia.
20,00 - Mesa redonda. Las construcciones en tierra cruda.
José Luis Saez Guerra, Vicerrector de Comunicación e Instalaciones, Universidad de Valladolid. Antonio Coronel, Licenciado en Arte, Gerente de ARESPA;
Pedro Martinez Massa, Presidente de la Fundación Española de Artesanía;
Antonio De Las Casas, Gerente de CEHOPU;
Juan José Arenas, Profesor de la Escuela de Ingenieros de Caminos, Santander.

SABADO-26 AMAYUELAS DE ABAJO (Palencia)
10,00 - Ponencia - Soluciones para la restauración con Adobe. BAHLA, Sultanato de OMAN, Hubert Guillaud, arquitecto. CRATERRE, Grenoble.
11,30 - Visita proyecto casas de tierra en Amayuelas,
M.J. González/ J. Silva/ F. Valbuena, arquitectos. Jon Santibáñez, bioconstructor.
12,30 - Experiencia de Córcega (Italia) sobre construcción con tierra,
María Spano, arquitecto.
16,00 - Retrospectiva construcción con tierra en Tierra de Campos,
Carlos Carricajo, arquitecto técnico.
17,00 - Visita Villa de la Olmeda y Pueblos de Tierra de Campos

DOMINGO-27 AMAYUELAS DE ABAJO (Palencia)
10,00 - Bioconstrucción y construcción con tierra cruda,
Ismael Caballero
11,00 - Métodos de trabajo en la construcción con tierra,
Beniamino Franco Atzori, alcalde de Tratalias (Italia). Ornella Bália, arquitecta.
12,00 - Métodos de diseño participativo,
Eric Gomez, arquitecto (México)
13,30 - Mesa redonda: Otras experiencias de construcción con tierra en Castilla y León.
Moderador, José Mª Sastre. Arquitecto Técnico (ASF CyL)
NAVAPALOS (Soria), BOCEGUILLAS (Segovia) y DIPUTACIÓN DE LEÓN.
14,30 - Inauguración viviendas de Tierra en Amayuelas: comida, fiesta..
16,30 - Debate - propuestas de acción para fomentar la construcción con TIERRA.
Moderador, Jerónimo Aguado, responsable CIFAES-Amayuelas de Abajo
18,00 - Conclusiones y clausura del encuentro

ACTIVIDADES COMPLEMENTARIAS EN AMAYUELAS DE ABAJO:

Viernes 25 de Mayo –
21 horas : FORO PARA EL DIÁLOGO Y LA EXPRESIÓN DE NUEVAS UTOPÍAS -
"El derecho de los/as Ciudadanos/as a una vivienda sana ", a cargo de GEA

ORGANIZA:

*CIFAES-AMAYUELAS DE ABAJO **
*CONSOZIO ECOSVLUPPO-MOMUNE DI TRATALIAS-CERDEÑA (ITALIA) **
CENTRO PARA LA RECUPERACIÓN DEL PATRIMONIO RURAL (ARQUITECTOS SIN FRONTERAS CASTILLA Y LEÓN)

PATROCINAN:

*COLECTIVO PARA EL DESARROLLO RURAL DE TIERRA DE CAMPPOS-INICIATIVA LEADER - 2 **
*COLEGIO DE APAREJADORES DE VALLADOLID **
FUNDACIÓN CAJA DE ARQUITECTOS

COLABORAN:

CAJA ESPAÑA,
REVISTA R&R,
HISPANIA NOSTRA,
FUNDACIÓN DEL PATRIMONIO DE CASTILLA Y LEÓN,
ESCUELA DE ARQUITECTURA DE VALLADOLID
CENTRO BUENDÍA, UNIVERSIDAD DE VALLADOLID

Información e inscripciones:
Centro de Investigación y Formación en Actividades Económicas Sostenibles (CIFAES).
Amayuelas de Abajo, 34429, Palencia.
Tfno 979 154022 y 979 154161. Fax: 979 154022. Email: amayuelas@cdrtcampos.es.

III JORNADAS SOBRE BIOCONSTRUCCIÓN Y VIVIENDA SOSTENIBLE

FIRA NATURA 8, 9 y 10 Marzo 2002

Datos de interés:

Lugar: *Sala de Congresos de la Fira de Lleida.*
Fecha: *Sábado 9 de Marzo del 2002, desde les 9.00 hasta las 20.30 h.*

Participantes y temas a tratar:

Alfonso Sevilla director de GEOHABITAT (Almeria), Energía y Medio Ambiente S.A.consultor-proyectista de la ciudad de Kronsberg (Alemania).

Pere Armengol arquitecto jefe de HABIOCLIMA (Lleida), gabinete especializado en arquitectura bioclimática e ingeniería sostenible.

Erick Gomez arquitecto de TIERRA CRUDA (Palencia) y coordinador del Projecto de Amayuelas de Abajo (Palencia).

Stefan Natke asesor en materiales de Bioconstrucción de BIOHAUS (Guipúscoa).

Mateu Ortoneda especialista en Bioconstrucción con dilatada experiencia internacional.

Pilar Valero decoradora especializada en construcción natural de BIOCE (Valencia)

Jordi Badia arquitecto de La Ciutat Verda (Barcelona) y miembro de la Fundación GEA

Toni Marín coordinador de la revista REHABITAR y de la Fundación GEA

Valentina Marini arquitecto de AraB

Horst Moritz asesor de materiales ecológicos de La Casa Ecològica (Tarragona)

*Este año presentamos dos casos **de actuaciones urbanísticas sostenibles** de primer nivel salvando sus peculiaridades diferenciadoras. El primer caso analizado se trata de la construcción de un barrio ecológico en un pueblo de Palencia utilizando materiales de la bioregión. La segunda nos acerca a la realidad de grandes modelos urbanos sostenibles como es el caso de Kronsberg en Alemania, una nueva ciudad anexa a Hannover. En esta actuación se pueden contemplar todas les fases del proceso del diseño utilizado y las posibilidades de aplicarlo en nuestra tierra.*
*Por lo que concierne a los materials usados en Bioconstrucción, este año se prioriza las soluciones constructivas basades en dos materials fonamentales a la Península Ibérica: **la tierra y la madera**.*
*Para concluir las jornadas se presentarán la revista sobre Bioconstrucción, Permacultura y Vida Sostenible REHABITAR y un par de **libros** con recursos para diseñar en las nuestras zonas cálidas y utilizar materiales naturales.*

PROGRAMA DEL TALLER SOBRE TIERRA
LA TIERRA MATERIAL DE CONSTRUCCIÓN.
18 AL 20 DE ABRIL DE 2002

V Curso de Especialización- Cooperación para el desarrollo de asentamientos humanos en el tercer mundo.

Escuela Técnica Superior de Arquitectura
Universidad Politécnica de Madrid

TALLER TEÓRICO- PRÁCTICO:

EN EL CENTRO DE INVESTIGACIÓN DE ARQUITECTURA TRADICIONAL- CIAT - BOCEGUILLAS (SEGOVIA).
Colaboración con el Departamento de Construcción y Tecnología Arquitectónicas – ETSA –UPM

DÍA	***HORARIO LECTIVO***	***TIPO DE ACTIVIDAD / TEMA***	***PONENTE***	***RESPONSABLE***
Jueves 18.04	*16:00 – 18:00*	*-Preparación de ensayos* *-Elaboración de Bloques de tierra compactada.*	*Gabi Barbeta* *Ignacio Oteiza*	*Ignacio Oteiza*
	18:00 - 20:00	*Visita Construcción con tierra.* *Centro de turismo rural- Covachelas- Sepúlveda.*	*Gabi Barbeta*	
Viernes 19.04	*9:00 – 10:30*	*La importancia de los materiales en los proyectos de construcción en el Tercer Mundo.*	*Julián Salas*	*Julián Salas*
	10:30 – 12:00	*La tierra material de construcción en el Tercer Mundo.*	*Mariano Vázquez ETSAM*	
	12:00 – 12:30	*Receso*		
	12:30 – 14:30	*Trabajos prácticos con tierra.* *Realización de ensayos.*	*Gabi Barbeta* *Ignacio Oteiza*	
		ALMUERZO		
	16:00 –17:30	*Construyendo con tierra: Proyecto de la ciudad Segundo Montes de El Salvador*	*Gabi Barbeta*	
	18:00 – 19:30	*Cinco saltos tecnológicos en las construcciones con tierra.* *(La tierra ante el sismo y el agua)*	*Julián Salas*	
	19:30 -	*Presentación del Centro de Investigación de Arquitectura Tradicional – CIAT – Boceguillas* *COLOQUIO GENERAL*	*Fernando Vela C.* *Luis Maldonado (Moderador) ETSAM*	
		CENA *Ofrecida por CIAT- Boceguillas*		
Sábado 20.04	*10:00 – 13:00*	*Participación en trabajos prácticos con tierra.* *Proyección de videos de construcciones con tierra*	*Gabi Barbeta* *Ignacio Oteiza*	*Ignacio Oteiza*
	13:30	*ALMUERZO* *Fin del Taller*		

V CURSO DE ESPECIALIZACIÓN

ESCUELA TÉCNICA SUPERIOR DE ARQUITECTURA. UNIVERSIDAD POLITÉCNICA DE MADRID
DIRECCIÓN: ***JULIÁN SALAS (DR. INGENIERO INDUSTRIAL****)* *Y* ***FELIPE COLAVIDAS (DR. ARQUITECTO).***
PATROCINADORES: ***MINISTERIO DE FOMENTO, CONSEJERÍA DE OBRAS PÚBLICAS Y TRANSPORTES DE LA JUNTA DE ANDALUCÍA, ARQUITECTOS SIN FRONTERAS, INSTITUTO JUAN DE HERRERA (E.T.S.A.M.) e INSTITUTO DE COOPERACIÓN PARA LA HABITABILIDAD BÁSICA*** *(en formación)*

COOPERACIÓN PARA EL DESARROLLO
DE ASENTAMIENTOS HUMANOS EN EL TERCER MUNDO
INSTRUMENTOS DE PLANEAMIENTO URBANO Y ALOJAMIENTO PARA AMÉRICA LATINA Y ÁFRICA

(Madrid, del 11 de enero al 25 de mayo de 2002)

PROGRAMA DEL TALLER
SOBRE TIERRA

TALLER TEÓRICO-PRÁCTICO: EN EL CENTRO DE BOCEGUILLAS (SEGOVIA), DEL 18 DE ABRIL AL 20 DE ABRIL CON LA COLABORACIÓN DEL DEPARTAMENTO DE CONSTRUCCIÓN DE LA ETSAM
LA TIERRA MATERIAL DE CONSTRUCCIÓN DEL TERCER MUNDO

DÍA	***HORARIO LECTIVO***	***TIPO DE ACTIVIDAD / TEMA***	***PONENTE***	***RESPONSABLE***
Jueves 18.04	*16:00-20:00*	*Preparación de ensayos y de trabajos prácticos con tierra (*)*	*Gabi Barbeta, UdG* *Ignacio Oteiza*	*Ignacio Oteiza*
Viernes 19.04	*9:00-10:30*	*La importancia de los materiales en los proyectos de construcción en el TM*	*Julián Salas*	*Julián Salas*
	10:30-12:00	*La tierra material de construcción del TM*	*Mariano Vázquez, ETSAM*	
	12:30-14:30	*Trabajos prácticos con tierra y realización de ensayos (**)*	*Gabi Barbeta, UdG* *Ignacio Oteiza*	
	16:00-17:30	*Construyendo con tierra proyecto de la Ciudad Segundo Montes del Salvador.*	*Gabi Barbeta, UdG*	
	18:00-19:30	*Cinco saltos tecnológicos en las construcciones con tierra* *(la tierra ante el sismo y el agua)*	*Julián Salas*	
	19:30	*Presentación del Centro de Boceguillas por Fernando Vela* *Coloquio general* *Moderador: Luis Maldonado, Catedrático ETSAM* *Cena Ofrecida por el Centro de Investigación de Arquitecturas Tradicionales de Boceguillas*		
Sábado 20.04	*10:00-13:00*	*Proyección de vídeos de construcciones con tierra y/o participación en trabajos prácticos con tierra y ensayos (***)*	*Gabi Barbeta, UdG* *Ignacio Oteiza*	*Ignacio Oteiza*
	13:30	*Almuerzo de fin del taller*		

(*)
1- Método de análisis de tierras para su estabilización y control.
2- Taller práctico de técnicas de ejecución : ejecución de un pequeño Tapial-
3.- La ejecución de adobes y BTC por parte de cada alumno. Ejecución de arco, como arranque de bóveda núbia
(**) Ejecución comentada e interpretación de los ensayos de laboratorio / Participación activa de los asistentes en la ejecución de la construcción iniciada.
(***) Sesión de proyección de vídeos sobre construcciones con tierra. En paralelo con las proyecciones, continuación de la ejecución de la construcción experimental

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