

## DYNAMIC SOIL CLAYS

*Derek C. BAIN*

*The Macaulay Institute, Craigiebuckler, Aberdeen AB15 8QH, UK Corresponding author's e-mail: d.bain@macaulaz.ac.uk*

*Only the abstract of this contribution, that was scheduled as the invited lecture in the XVIIth Conference on Clay Mineralogy and Petrology, is here published. The author assumes that full text of this lecture at the meeting is not appropriate for printing in Proceedings, as his talk was mostly about other peoples work.*

### Abstract

Soil clays, particularly expansible phases such as smectite and vermiculite, are very sensitive to the environment in which they occur and to any changes which occur to that environment.

Because of the nature of the interlayer region, hydroxy-interlayered vermiculite and smectite are highly variable and changes in environmental conditions can be reflected in the degree of interlayer filling and in the relative stability of the interlayer components. Lowering of the soil pH by acid precipitation or change of land use such as planting of trees on former arable land can result in the interlayer material being removed from hydroxy-interlayered phases.

Modifications to hydroxy-interlayered clays are easily detected by conventional X-ray diffraction (XRD) techniques but more sophisticated XRD peak analyses routines are needed to detect more subtle changes in soil clay mineralogy. Application of such techniques to soils has shown that soil clays are dynamic systems which can change in quite short periods of time, as little as 30 years. Some examples of such changes will be presented.

Two weathering trends were established in a series of three brown forest soils in close proximity but under different land uses in Scotland:

(1) an increasing proportion of vermiculite in interstratified mica-vermiculite in the upper horizons of the arable and forested soils;

(2) formation of high-charge corrensite by weathering of chlorite in all three profiles but least pronounced in the arable soil. The differences in clay mineralogy amongst the profiles are minor, but these two different weathering trends may be due to the effects of different land use.

Research using methods to decompose XRD patterns of soil clay fractions from soils taken between 1913 and 1996 from agricultural experimental plots in the USA suggest that there is a significant influence of cropping method on the soil clays. Little change in clay mineralogy was seen in the rotation plot but there was a significant loss of illitic material from different phases for the plots with continuous corn cultivation. Use of NPK fertilizer since 1955 appears to have restored the clay mineralogy for the soils in continuous cropping compared to that for the 1913 samples.

Loss of K-bearing clay minerals such as discrete illite and interstratified mica layers and an increase in the formation of chlorite have been recorded in Chinese rice paddies, the changes occurring over 30 years or less.

In a chronosequence of poldered sediments in France, the natural mineral suite of kaolinite, mica, illite and two disordered illite-smectite phases have changed gradually but significantly over time to a more smectitic clay assemblage.

These examples indicate that clay minerals in soils are dynamic systems that are affected by changes to their environment. Some changes to the clays are reversible but other changes can be irreversible.

## THE PRELUDE OF PORCELAIN IN PORTUGAL

**Celso GOMES**

*MIA (Centro de Investigação "Minerais Industriais e Argilas") da FCT (Fundação para a Ciência e a Tecnologia), Universidade de Aveiro, 3810-193 Aveiro, Portugal*

*Corresponding author's e-mail: cgomes@geo.ua.pt*

*Only the abstract of this contribution, that was scheduled as the invited lecture in the XVIIth Conference on Clay Mineralogy and Petrology, is here published. The author is preparing for publication an extended text with the same title of his lecture at the meeting as a book a Portugal.*

### Abstract

The Portuguese were the first to introduce and commercialise in Europe the porcelain produced in China, where this interesting utilitarian and decorative type of ceramics has been produced, at least since 400 a.C, being the initial productions entirely reserved for the emperor's palace. Within the Europeans the Portuguese were in the last positions concerning the porcelain manufacture in industrial terms. The industrial production of porcelain has started in 1710 in Meissen (Germany), in 1727 in Sèvres (France) and in 1746 in Plymouth (England). As a matter of fact, the first porcelain industrially produced in Portugal have taken place in 1834, at the Fábrica de Porcelanas Vista Alegre, located in Ílhavo, a small town located nearby the town of Aveiro. The factory was founded in 1824 by José Ferreira Pinto Basto. Vista Alegre porcelain is commercialised world-wide being distinguished by its excellent quality and design. The production of hard porcelain or Chinese porcelain did represent an important scientific, technological and cultural revolution in all the European kingdoms. As a matter of fact, porcelain manufacture did represent the transition from the empirical to the scientific concern, in the area of ceramic materials. In Portugal, about fifty years before the industrial production of porcelain that was carried out in 1834 by Fábrica Vista Alegre, several laboratory tests have been carried out in Lisbon, regarding the production of hard porcelain. Such tests took place, in the period 1773-1783, undertaken by the lieutenant-general Bartholomeu da Costa, member of the Academy of Sciences of Lisboa, and they were carried out at the Laboratories of Guns and Instruments of the Artillery Foundries.

Some of the pieces (medals/cameos) made of porcelain that have been produced by Bartholomeu da Costa are part of the museum collections of the Academy of Sciences of Lisboa, being stored, preserved and exhibited in the Council Room or Dona Maria I Room. We looked at and analysed porcelain pieces whose manufacture is attributed to Bartholomeu da Costa, some belonging to the Academy of Sciences of Lisbon, others belonging to the private collection. Within all the studied porcelain pieces, four of them produced both in 1773 and in 1775, were selected based on the extraordinary quality of the porcelain and on the peculiarities shown by their respective compositions. As a matter of fact, some mineral raw materials, such as talc and calcite, which are not part of the porcelain formulations currently produced, have been incorporated in the ceramic pastes. The results of analyses being carried out on those four selected porcelain pieces are herewith disclosed. X-ray micro-diffraction was the principal analytical technique being employed, allowing the identification of the high temperature crystalline phases (mullite, quartz, cristobalite, cordierite and diopside) and the presence of glass. Plates containing photographs revealing the peculiar morphological features of the studied porcelain pieces are presented too.

**CHARACTERIZATION AND POTENTIAL APPLICATION OF PLIOCENE CLAYS FROM MENZEL TEMIME REGION (NORTH EAST OF TUNISIA) FOR BRICK AND FAIENCE CERAMICS FABRICATION**

***Islem CHAARI*<sup>1)</sup>, *Emna FAKHFAKH*<sup>1)</sup>, *Mondher HACHANI*<sup>2)</sup>, *Rabah ALOUANI*<sup>3)</sup>, *Mounir MEDHIOUB*<sup>3)</sup>, *Fethi KOOLI*<sup>4)</sup> and *Fakher JAMOUSSE*<sup>1)\*</sup>**

<sup>1)</sup> *Laboratoire de Géoresources INRST BP 95, 2050 Hammam – Lif, Tunisia*

<sup>2)</sup> *Département de géologie. Faculté des Sciences de Bizerte, 7021 Zarzouna, Bizerte, Tunisia*

<sup>3)</sup> *Département des Sciences de la terre. Faculté des sciences de Sfax, Tunisia*

<sup>4)</sup> *ICES, 1Pesek Road, Jurong Island 62 7833. Singapore*

*\*Corresponding author's e-mail: Fakher.Jamoussi@inrst.rnrt.tn*

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**Abstract**

The Pliocene in Menzel Temime region (Northeast of Tunisia) overlying the Saouaf formation of Middle Miocene age, is represented by three lithostratigraphic formations: Potter clays, sand of Nabeul and Sidi Barka clays. Clay fractions consist of kaolinite and illite with plastic properties and minor quartz, calcite and feldspar. Applications of clays in bricks and faience ceramics are reported. However, the resulting faience ceramics exhibit some textural defects. These defects could be eliminated by increasing of pressure of the mold.

**KEYWORDS:** clay, valorization, Pliocene, ceramic, Tunisia

**TUNISIAN SMECTITIC CLAYS AS RAW MATERIALS FOR THE PRODUCTION**

## OF LIGHTWEIGHT AGGREGATES

**E. FAKHFAKH<sup>1\*</sup>, Islem CHAARI<sup>1)</sup>, M. MEDHIOUB<sup>2)</sup>, F. ROCHA<sup>3)\*</sup>, Celso GOMES<sup>3)</sup>,  
J. MARQUES<sup>4)</sup>, J. COROADO<sup>5)</sup>, Alberto LOPEZ-GALINDO<sup>6)</sup>, Fethi KOOLI<sup>7)</sup>, F.  
ZARGOUNI<sup>8)</sup> and Fakher JAMOUSSE<sup>1)\*</sup>**

<sup>1)</sup> Laboratoire de Géoresources INRST BP 95, 2050 Hamam-Lif, Tunisia,

<sup>2)</sup> Département des Sciences de la Terre, Faculté des Sciences de Sfax, Tunisia

<sup>3)</sup> Univ. Aveiro, Campo de Santiago, 3810 Aveiro, Portugal

<sup>4)</sup> Centro tecnologico da Cerâmica e do vidro, Rua Coronel Veiga Sima, 3000 Coimbra

<sup>5)</sup> MIA-Centro de Investigação "Minerais Industriais e Argilas" da Fundação para a Ciência e a Tecnologia (FCT), Instituto Politécnico de Tomar

<sup>6)</sup> IACT.CSIC-Univ. Granada. Avda. Fuentenueva, 18002-Granada, Spain

<sup>7)</sup> ICES, 1Pesek Road, Jurong Island 62 7833. Singapore

<sup>8)</sup> Département de Géologie. Faculté des Sciences de Tunis. 1060 Belvédèr, Tunisia

\*Corresponding author's e-mail: Fakher.Jamoussi@inrst.rnrt.tn, frocha@geo.ua.pt

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### Abstract

Smectitic clays from 12 deposits located in the Meridional Atlas domain (Tunisia) are explored for manufacturing of expanded aggregates. Two types of firing processes (slow and quick firing) were carried out, and properties of the bloated products were examined. Used raw materials are mainly composed of smectite, kaolinite and illite phases with quartz, calcite, dolomite and feldspars as impurities. They contain high amounts of fluxes ( $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ) with  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$  dominating others. Quick firing or "flash heat" must be preceded by two hours drying at  $350^\circ\text{C}$  in order to avoid any aggregate explosion which seems to be related to the fineness of a raw material. The clay fineness appears to be the cause of ball explosion. Clay aggregates were heated at the maximum bloating temperature ( $1170^\circ\text{C}$ ) during 5 min. and then characterized through a determination of the apparent density, the mechanical resistance corresponding to the rupture under point compression, and water absorption measured after 72 hours of immersion in distilled water. Obtained results are encouraging and may open new perspectives for the utilization of some investigated smectitic clays in civil construction works.

**KEYWORDS:** smectite, light weight aggregate, firing processes, apparent density, Meridional Atlas domain, Tunisia

## **SMECTITE FOR HUMAN HEALING USE**

**Emna FAKHFAKH**<sup>1)</sup>, **Ibticem CHAKROUN**<sup>1)</sup>, **Islem CHAARI**<sup>1)</sup>, **Mounir MEDHIOUB**<sup>2)</sup>,  
**Fernando ROCHA**<sup>3)\*</sup>, **Celso GOMES**<sup>3)</sup>, **Alberto LOPEZ-GALINDO**<sup>4)</sup>, **Fethi KOOLI**<sup>5)</sup>,  
**Fouad ZARGOUNI**<sup>6)</sup> and **F. JAMOUSSE**<sup>1)\*</sup>

<sup>1)</sup> *Laboratoire de Géoresources INRST BP 95, 2050 Hamam-Lif Tunisi, Tunisia*

<sup>2)</sup> *Département des Sciences de la Terre, Faculté des Sciences de Sfax, Tunisia*

<sup>3)</sup> *Univ. Aveiro, Campo de Santiago, 3810 Aveiro, Portugal*

<sup>4)</sup> *IACT.CSIC-Univ. Granada. Avda. Fuentenueva, 18002-Granada, Spain*

<sup>5)</sup> *ICES, 1Pesek Road, Jurong Island 62 7833, Singapore*

<sup>6)</sup> *Département de Géologie. Faculté des Sciences de Tunis. 1060 Belvédère. Tunis, Tunisia*

*\*Corresponding author's e-mail: frocha@geo.ua.pt, FakherJamoussi@inrst.rnrt.tn*

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### **Abstract**

The use of clays for therapeutic purposes is mainly related to their high absorbent and adsorbent properties. In dermatology and cosmetics (topical applications), clays are used due to their high swelling, high plasticity, high specific surface and high ion exchange properties. In this paper, mineralogical, chemical and technological properties of some Tunisian smectitic clays are reported with the aim to assess their suitability to be used for therapeutic external applications. Properties of these clays have been compared to those of the bentonite of Porto Santo Island (PSBT) of the Madeira archipelago (Portugal), considered to be very interesting for therapeutic treatment on the basis of their technological characterization (CEC, specific surface, exchangeable cations, specific heat, cooling rate and abrasivity). Among the investigated clays the HMD1, TFL1, BRD1 and AYD1 seem to be the most appropriate for topical applications as cataplasms or mud baths.

**KEYWORDS:** smectite, cooling kinetic, specific heat, topical application, Atlas domain, Tunisia

## **PHYSICO-CHEMICAL MECHANICS OF CLAYS' SWELLING**

**Maxim G. KHRAMCHENKOV**\*, **Eduard M. KHRAMCHENKOV**  
**and Nikolai B. PLESHCHINSKII**

*Kazan State University, Universitetskaya 17, 420008 Kazan, Russia*

*\*Corresponding author's e-mail: mkhramch@ksu.ru*

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### **Abstract**

The mathematical model of swelling systems rheology is considered. As a basis of a model the generalization of the theory of consolidation was used on a case when the mass of a solid phase of a porous skeleton changes due to an overflow of a fluid during processes of swelling / shrinkage under action of osmotic pressure. The problem of swelling / shrinkage of a clay layer is put and solved. On the basis of the analysis decision features of a model, important for the explanation of some characteristic features of processes in swelling systems are investigated. It is shown, that the received decisions, are in the good consent with results of experiments.

**KEYWORDS:** clays, swelling, rheology, mathematical model

**CLAY MINERALS INCLUDING RELATED PHYLLOSILICATES:**

## INTERDISCIPLINARY RESEARCH AND INWARD INTEGRATION

**Jiří KONTA**

*Professor Emeritus, Faculty of Sciences, Charles University, Albertov 6, 128 43 Prague 2*

*home address: Korunni 127, 13000 Prague 3, Czech Republic*

*Corresponding author's e-mail: petrol@natur.cuni.cz*

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### Abstract

More than 110 species of clay minerals and related phyllosilicates were discovered mostly in the 20<sup>th</sup> and 19<sup>th</sup> centuries, including 13 regular interstratifications (R1 range) naturally occurring or synthesized and referred to between 1950-2003. This contribution to theoretical and applied clay science, whose evolution is based on mineralogical roots, stresses interdisciplinary research among clay science, basic sciences (physics, chemistry, mathematics, geometry), earth-, biological-, applied- and related sciences and engineering technologies as a basis for substantial past and future discoveries. Not only a novel desirable cooperation with other theoretical and applied disciplines, but also a close inward integration among the six major research regions of clay science is necessary for its further development. Two diagrammatic presentations show:

- 1) a desirable multidisciplinary cooperation and mutual influence among sciences and technologies affecting the development and progress of clay science;
- 2) a view of desirable integration among the six major research regions within clay science in the near future.

**KEYWORDS:** theoretical and applied clay science, history, names of clay mineral species and related phyllosilicates (more than 110), research regions and subregions, interdisciplinary cooperation, desirable inward integration

**EXPANSIVE CLAYS IN TRACK SUBGRADE IN DEEP CUT (SECTION**

## TŘEBOVICE – RUDOLTICE, CZECH REPUBLIC)

*František KRESTA*

*Stavební geologie – Geotechnika a.s., branch Ostrava, 28.října 150, 702 00 Ostrava – Moravská Ostrava,*

*Czech republic, tel./fax : 00-420-597577677, MT : 00-420-602-342896*

*Corresponding author's e-mail: kresta@geotechnika.cz*

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### Abstract

Track section Třebovice – Rudoltice on the border between Bohemia and Moravia and European watershed is one of the most complicated sections in Czech Republic. Main difficulties in that area result from expansive clays with high plasticity. Swelling of these clays caused destruction of the Třebovice tunnel built in 1842. This tunnel was restored after great difficulties in 1932.

Modernisation of railway track in that area was solved by re-alignment of existing tracks. Crossing the soils with the worst mechanical properties (highly plastic expansive clays) was designed as cut-and-cover double-track tunnel protected by diaphragm walls with invert. Contractor that won the tender suggested solution with open cut and proclaimed significant reduction of costs. Geotechnical hazards of this alternative were discussed in paper in Railway Engineering 2003.

Expansive clays occurring at the bottom of this cut (depth of 12 m) represent the most significant geotechnical hazard. We had a short time to analyse behaviour of these expansive clays, to find out any relationships and to define and make trial tests of their treatment. Expansive clays in that area are represented by marine Miocene highly plastic clays (CV, CE) that are stiff to firm (unconfined shear strength is 200-300 kPa.). Linear swelling achieves values up to 25 % (median is 5 %); the maximal value of swelling pressure was 276 kPa (median is 111 kPa.).

It is mainly organic matter dispersed within clays that causes swelling of them. The organic matter content is 4-7 %, maximally 12 %. Influence of mineralogical composition of clays on their swelling behaviour has not been proven.

Due to time shortage only two methods of expansive clays treatment were tested. In both cases we considered mixing of clay in situ with a binding agent and in one case we added also granular aggregates. By comparing linear swelling and swelling pressures of untreated and treated samples we obtained the best result for treatment of clay by lime (5 %), cement (7 %) and gravel fraction 0-4 mm (10 %). In case of treatment only by lime (8%) and cement (7 %), linear swelling was higher than in treatment by the first mixture.

CBR values of treated materials increased from 6-8 % to 25-30 %. Similarly its shear strength parameters changed (effective cohesion increased from 5 kPa to 40 kPa).

Based on our laboratory study, the treatment of expansive clays on the bottom of the deep cut and in track subgrade was proposed.

**KEYWORDS:** expansive clays, Miocene, swelling, Třebovice-Rudoltice, geotechnical hazard, mineral composition, organic matter

**EXPERIMENTAL STUDY AND MATHEMATICAL MODELING OF Cs (I) AND Sr**

## (II) SORPTION ON BENTONITE AS BARRIER MATERIAL IN DEEP GEOLOGICAL REPOSITORY

*Helena KROUPOVÁ<sup>1)</sup>\* and Karel ŠTAMBERG<sup>2)</sup>*

*<sup>1)</sup> Centre for Radiochemistry and Radiation Chemistry, CTU, Břehová 7, 115 19 Prague 1*

*<sup>2)</sup> CTU, Faculty of Nuclear Science and Physical Engineering, Dpt. of Nuclear Chemistry, Břehová 7, Prague 1*

*\*Corresponding author's e-mail: kroupova@jffi.cvut.cz*

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### Abstract

The migration of radionuclides through bentonite barrier in deep geological repository is strongly influenced by sorption processes. In our deep geological repository in granite massif, the canisters made of stainless and carbon steel and compacted bentonite barrier are planned. The experimental investigation on sorption processes in such system and their appropriate mathematical description including observation of a main corrosion product of the canister wall (namely the magnetite) were the aim of this work.

Based on own experiences and literature data, we arranged batch experiments in PE vials. The experimental systems consisted of: (i) synthetic granitic water with a given ionic strength ( $\text{NaNO}_3$ ) and concentrations of studied radionuclides ( $10^{-6}$  mol/l  $\text{CsCl}$  or  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  spiked with  $^{137}\text{Cs}$  or  $^{85}\text{Sr}$ ); (ii) pre-treated (with the aim to remove carbonates) bentonite suspension, magnetite and their mixtures. The experimental data were modeled using: (i) surface complexation models for edge sites, namely, two electrostatic – Diffusion Double Layer Model (DLM) and Constant Capacitance Model (CCM) – and Chemical Model (CEM), without an electrostatic correction, (ii) ion exchange model (IExM) for layer sites. The corresponding program package was developed (STAMB-2003). Sorption and protonation parameters were obtained by fitting of appropriate experimental data. The quality of fit was evaluated by means of the WSOS/DF criterion, the values of which should be lower than approx. 20.

In the first modeling step, the interaction of protons and hydroxyl ions with the solid phases was investigated by alkalimetric and acidimetric titrations under exclusion of  $\text{CO}_2$  (under  $\text{N}_2$  atmosphere) for ionic strengths of background electrolyte 0.1 and 0.01 ( $\text{NaNO}_3$ ). On the basis of WSOS/DF criteria values and the meaningful values of the parameters, the CEM model and the ion exchange model (IExM), were chosen and the corresponding values of the protonation constants, total concentration of edge sites, cation exchange constants, total concentration of layer sites were obtained and used for further calculations.

In the second modeling step, the percentage of sorption of Cs(I) and Sr(II) as a function of pH was determined under oxic conditions at room temperature. During 28 - day period (28 days are required for equilibrium establishment) the pH of the system was five times adjusted to the pH value required. Then phases were separated by centrifugation and the equilibrium concentrations in solution were determined. The experimental data of sorption were fitted by CEM+IExM and the corresponding averaged values of sorption constants, including the WSOS/DF, were obtained. These sorption parameters, and parameters mentioned above, were successfully used for simulation calculations of pH-dependences of sorption based on two modeling approaches, namely on so called GC (Generalized Composite) and CA (Component Additivity) approaches.

It has been found that: (i) bentonite is an efficient sorbent for Cs(I) and Sr(II), (ii) the reactions taking place on layer sites of bentonite play the most important role in the sorption process, mainly in the case of Cs, (iii) bentonite is much better sorbent than magnetite, (iiii) the system can be successfully modeled using surface complexation model type of CCM in combination with ion exchange model.

**KEYWORDS:** barriers, bentonite, magnetite, sorbent, radionuclides, titrations

**THE KAZAKHSTAN CLAY FOR DRILLING MUDS**



**Gulzhan A. KUDAIKULOVA <sup>1)</sup>\*, Heike STRAUSS <sup>2)</sup> and Volker KOECKRITZ <sup>2)</sup>**

<sup>1)</sup> Kazak National Technical University, Satpaev str. 22a, Almaty, Kazakhstan

<sup>2)</sup> Technical University of Freiberg Mining Academy, Agricolastrasse 22, 09599 Freiberg, Germany

\*Corresponding author's e-mail: kgulzhanabd@mail.ru

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#### Abstract

This paper presents the results of studying the physical–chemical, physical–mechanical, structure–mechanical and technological properties of Kazakhstan bentonite clay of Taganskoye deposit.

**KEYWORDS:** bentonite, montmorillonite, Kazakhstan, deposits, mineralogical and granulometric composition, physical and chemical properties

### **XRD OF WET SPECIMEN – SOURCE OF INTERESTING INFORMATION**

**Radko A. KÜHNEL <sup>1)</sup>\* and S. J. VAN DER GAAST <sup>2)</sup>**

<sup>1)</sup> Delfgauw, The Netherlands

<sup>2)</sup> Royal Netherlands Institute for Sea Research (NIOZ), P. O. Box 59, 1790 AB Den Burg, Texel, the Netherlands

\*Corresponding author's e-mail: r.kuhnel@hetnet.nl

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#### Abstract

Some minerals, particularly clay minerals, are humidity sensitive. Expansion and shrinkage of clays is caused by interaction with water. Changes of volume of clay masses endanger engineering structures of any kinds, buildings, road and waterworks. Besides threatening actions, expanding clays find numerous applications for instance as sealing material, packing material and as drilling fluids. In laboratories, expandability of clays is frequently studied by means of X-ray powder diffraction (XRD) of hydrated or glycolated specimens. Although hydration is a natural process a majority of researchers prefers glycolation rather than hydration. Generally, the examination of wet clay brings more information and improves understanding of clay behaviour. If the impact of humidity on smectite is disregarded, misinterpretation of XRD patterns can happen. That concerns mainly the detection of mixed layer clay minerals. Comparison of hydration and glycolation of smectite is discussed. Examples of hydration of a few smectites, a halloysite and an illite are given.

**KEYWORDS:** X-ray, powder diffraction, clay minerals, smectite, humidity, hydration, glycolation, swelling

### **STRUCTURE OF VERMICULITE MODIFIED BY ORGANIC MOLECULES**

**Jiří MALIŠ<sup>1)\*</sup> and Monika KŘÍSTKOVÁ<sup>2)</sup>**

<sup>1)</sup> Faculty of Mining and Geology, Technical University Ostrava, 708 33 Ostrava - Poruba, Czech Republic

<sup>2)</sup> Institute of Materials Chemistry, Technical University Ostrava, 708 33 Ostrava - Poruba, Czech Republic

\*Corresponding author's e-mail: [jiri.malis@vsb.cz](mailto:jiri.malis@vsb.cz)

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#### Abstract

Intercalation of vermiculites by organic molecules is connected with an expansion of the structure in the direction vertical to the layers. Rate of expansion depends on the length of intercalated molecules, on their arrangement in an interlayer space and also on their concentration and reaction time. Natural Mg-vermiculite from Letovice location in the Czech Republic (VER-L) with the mean particle diameters equal to 194  $\mu\text{m}$  and coarse grained Mg-vermiculite from Santa Olalla location in Spain (VER-S) with size of flakes up to 5 mm were used as hostes for intercalation. Three organic molecules with different length of chains were used as intercalants: octadecylamine, dodecylamine, octylamine. Intercalation was carried out by low temperature heating procedure at the temperature of 80  $^{\circ}\text{C}$  lasting 24 hours. Molar ratio of vermiculites to organic molecules was 1:6 in all samples. The XRD patterns of all intercalated samples exhibit significant changes in comparison with the patterns of non-treated vermiculites. The patterns of vermiculites intercalated by octadecylamine molecules (18 C atoms) contain the integral set of basal diffractions with d-spacings 58.4  $\text{\AA}$ , 29.3  $\text{\AA}$ , 19.5  $\text{\AA}$  for VER-L or 51.9  $\text{\AA}$ , 25.6  $\text{\AA}$ , 17.2  $\text{\AA}$  for VER-S respectively. The differences in d-spacings depend on the size of flakes. Intercalation by dodecylamine (12 C atoms) was nearly the same with both vermiculites and XRD pattern contains the set of basal diffractions 38.7  $\text{\AA}$ , 19.7  $\text{\AA}$ , 13.6  $\text{\AA}$ . The result of intercalation by octylamine (8 C atoms) is not very significant. Just one basal diffraction value namely 19.7  $\text{\AA}$  for VER-L and 24.7  $\text{\AA}$  for VER-S was recorded. The surface of VER-S flakes after intercalation was observed using atomic force microscopy technique. Nano-layers of organic molecules chains grafted during the intercalation process were found on the surface. The graft does not cover the whole surface of flakes homogenously creating the irregular net of chains with different widths. Their shape and position is influenced either by distribution of electric charge on the surface or by surface folding caused by partial dehydration of Mg-vermiculite at the temperature of 80  $^{\circ}\text{C}$ .

**KEYWORDS:** vermiculite, intercalation, basal diffraction, organic molecules

## OF AQUEOUS-ALCOHOLIC SOLUTIONS

*Valerij V. MANK and L. N. MELNYK*

*National University of Food Technologies, Vladimirska, 68, Kiev, Ukraine*

*Corresponding author's e-mail: emerald\_era@hotmail.com, oloore@ua.fm*

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### Abstract

Clay minerals palygorskite and hydromica effectively sorb impurities worsening ethanol quality. Using of combined sorbents for clearing aqueous-alcoholic solutions appears to be necessary. Natural minerals palygorskite and hydromica are ecologically safe adsorbents.

**KEYWORDS:** sorbents, mordenite, clinoptilolite, montmorillonite, saponite, glauconite, hydromica, palygorskite, Ukrainian deposits, "sortovka"

## HYDROBIOTITE FROM THE DĚTAŇ OLIGOCENE TUFFS (DOUPOVSKÉ HORY Mts.)

*Karel MELKA \*, Jaromír ULRYCH and Radek MIKULÁŠ*

*Institute of Geology, Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Praha 6 – Lysolaje, Czech Republic*

*\*Corresponding author's e-mail: melka@gli.cas.cz*

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### Abstract

Oligocene tuffs in the quarry near Dětaň (Doupovské hory Mts.) contain short columns of dark mica reaching up to 15 mm in diameter. X-ray diffraction study revealed that their original phlogopite crystal structure was transformed during weathering processes into phlogopite-vermiculite structure. The dark mica from Dětaň, in comparison to the dark mica from the nearby Oleška locality, shows much simpler X-ray diffraction scheme. X-ray diffraction has found here only phlogopite and vermiculite components joined in mixed-layered forms, irregularly or regularly (hydrobiotites) arranged, beside preserved phlogopite parts of 2M1 structural type. DTA curve is similar to that of vermiculite. Thermogravimetry, however, exhibits lower amount of water in respect of this mineral, confirming the presence of the mixed-layer structure. Computer program Newmod simulated the arrangements with regular mixed-layer structure in hydrobiotite beside irregular interstratification of phlogopite and vermiculite sheets.

**KEYWORDS:** hydrobiotite, Dětaň, oligocene, mixed-layer structure

**Haydn H. MURRAY**

*Indiana University, Department of Geological Sciences, 1001 E. Tenth Street, Bloomington, Indiana 47405 USA*

*Corresponding author's e-mail: murrayh@indiana.edu*

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#### **Abstract**

Clay minerals that are used for absorbent and adsorbent applications are most commonly calcium montmorillonite and palygorskite. Calcium bentonite deposits are found in North and South America, Europe, Africa, and Asia in many locations on the above continents. Palygorskite occurrences are in North America, Africa, Europe, and Asia, but are much less common than calcium bentonite deposits. Because of their high surface area and lattice charge, these two clay minerals are good sorbents.

These minerals are mined and are normally dry processed but calcium bentonite is wet processed to produce high quality acid activated product for clarifying oils. These processes will be described.

Each of these two sorbent clays have multiple applications, the largest of which is cat litter. Other major uses are as oil and grease absorbents, carriers for agricultural chemicals, pesticides, and insecticides, and bonding agents for animal feed pellets. Other applications will also be discussed.

**KEYWORDS:** absorbents, calcium bentonite, hormites, acid activated clays

### **PHONOLITE WEATHERING PROFILES AT MARIÁNSKÁ HORA HILL, ČESKÉ STŘEDOHOŘÍ Mts., AND SORPTION PROPERTIES OF CLAY RESIDUES**

**Jiří K. NOVÁK<sup>1)\*</sup>, Karel MELKA<sup>1)</sup>, Jaromír ULRYCH<sup>1)</sup> and Zdeněk ŘANDA<sup>2)</sup>**

<sup>1)</sup> *Institute of Geology, Academy of Sciences CR, Rozvojová 135, 165 02 Praha 6, +420/233087241, fax +420/220922670*

<sup>2)</sup> *Institute of Nuclear Physics, Academy of Sciences CR, 250 68 Řež u Prahy, +420/266173156, fax +420/220941130*

*\*Corresponding author's e-mail: novak@gli.cas.cz*

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#### **Abstract**

Two exposed but incomplete paleoweathering profiles (without lateritic nodular crust and fossil topsoil cover), developed on phonolite at Mariánská hora Hill in Ústí nad Labem (U-II) and Ryzelský vrch Hill near Most in NW Bohemia, were studied by available laboratory methods. The special attention was paid to the sorption properties of weathering products. Their decolouring ability was used for practical purposes at the beginning of the last century. The saprock and green-coloured saprolite from the bottom part of both profiles host smectitic pseudomorphs after clinopyroxene, while the dominant feldspar components, such as anorthoclase and Na-sanidine, remained resistant to weathering. The cation exchange capacities (CEC) of green-coloured saprolite show high values. The uppermost white saprolite occurs as a result of kaolinitic replacement of feldspars and of the smectite-to-kaolinite transformation, with low CEC values. The additional importance of weathering processes is demonstrated by the mobility of REEs, e.g. of Ce in a white horizon ((Ce/Ce\*=1.21).

**KEYWORDS:** phonolite, weathering, saprolite, smectite, sorption, Mariánská hora Hill, NW Bohemia

**SOME PORTUGUESE CLAY SEDIMENTS USED AS RAW MATERIALS FOR**

## **CURATIVE CLAY PASTES: A STUDY OF PHYSICAL AND TECHNOLOGICAL PROPERTIES**

**Mario REBELO <sup>1)</sup>, Paulo GONÇALVES <sup>1)</sup>, Emilio SILVA <sup>2)</sup> and Fernando ROCHA <sup>1)</sup>\***

<sup>1)</sup> *Industrial Minerals and Clays Centre, Departamento de Geociências, Universidade de Aveiro, 3810-193 Aveiro, Portugal*

<sup>2)</sup> *ELMAS Research Centre, Departamento de de Geociências, Universidade de Aveiro, 3810-193 Aveiro, Portugal*

*\*Corresponding author's e-mail: frocha@geo.ua.pt*

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### **Abstract**

The assessment of mineralogical, physical and thermal properties of silt-clay fraction from several sedimentary rocks, aimed to the pelotherapy paste preparation, is presented. All clay separates commonly exhibit a higher clay fraction content (as a rule >50 wt %), despite different genesis (Jurassic, Upper Cretaceous and Miocene marly clay as well as marl, Miocene clayey sandstone and mudstone). After beneficiation, the majority of clay pastes can be suited for the use in pelotherapy, due to higher proportion of swelling Ca-smectite and mixed-layer illite/smectite among other clay minerals, such as illite, kaolinite, and chlorite. The clay pastes from Vimeiro 2 (smectite > kaolinite + illite) and that of Torres Vedras 6 (kaolinite > illite, smectite, interstratified illite-smectite) can be candidate materials. Their plasticity index (P.I. = 14-17 %), cation exchange capacity (CEC = 16 - 25 meq/100 g), higher water adsorption as well as low abrasivity index (0.16 - 0.19 mg/m<sup>2</sup>), low cooling rate (29 min.) and ease of handling are comparable with peloid properties commonly used in the Portuguese spas-centres. Moreover, Miocene marly clay from the locality Monfortinho shows a palygorskite admixture, the CEC of about 20.2 meq/100 g, and highest plasticity index (P.I. = 35). However, lower clay-sized proportion (36 %) and sand-sized particles reduce the stickiness on the skin and heat retention.

**KEYWORDS:** clay separates, physical-technological testing, pelotherapy, Portugal

**CALCITE CONCRETIONS IN TURONIAN MARLY SILICITES,**

## CENTRAL BOHEMIA

*Jan ŠRÁMEK*

*Při trati 1232, 141 00 Praha 4, Czech Republic*

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### Abstract

Calcite concretions from both Přední Kopanina (Prague suburb) and Hředle quarries were the subject of the reported study, or more exactly, insoluble residues from concretions occurring in totally decalcified lower Turonian "marly" silicites (opuka in Czech and Plänerkalk in German languages). Both localities belong stratigraphically to Bělohorské souvrství - Member of the Bohemian Cretaceous Basin.

Mutual comparison of chemical analyses recalculated to "normative" minerals reveals that in the course of diagenesis initial compositions of sediments have been changed remarkably. The original content of normative feldspars preserved in concretions and nodular beds ranges between 9.4 and 18.5 %, remarkably decreases to 4.3 - 10.6 % in host rocks affected by diagenesis. At the same time the content of clay and mica minerals (kaolinite, chlorite, illite or glauconite) in host sediments increases two or three times (from 7.3 - 11.2 % to 18.1 - 22.7 %). Comparison of concretions insoluble residues (I.R.) of concretions with decalcified host sediments from two quarries near village Hředle showed a different picture. The I.R. of concretions contain 10.2 - 25.3 % of feldspars comparing with 6.2 - 7.9 % in host sediments. However, the content of clay and mica minerals, which in I.R. of concretions forms about 28.8 - 33.9 %, decreases three up to five times (to 6.8 - 7.3 % content) in host rocks.

Reasons for this irregularity are supposed to be attributed to the late diagenesis and epigenesis, which not only completely remove calcite, but also dissolve feldspars and clay and mica minerals in host sediments. Microsparitic calcite concretions, which are much denser and less porous than the host rocks, preserve an original composition of the sediment, because the removal of calcite from them passed very slowly.

**KEYWORDS:** calcite concretions, Přední Kopanina, Turonian, diagenesis, clay and mica minerals, marly silicite

**Lenka VACULÍKOVÁ\* and Eva PLEVOVÁ**

*Centre of Geomaterials, Institute of Geonics, Academy of Sciences of the Czech Republic,  
Studentská 1768, CZ-708 00, Ostrava-Poruba, Czech Republic, Tel: +420-596 979 111, Fax:  
+420-596 919 452*

*\*Corresponding author's e-mail: vaculikova@ugn.cas.cz*

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#### **Abstract**

Real possibilities of FTIR-spectroscopy application along with thermal analysis (TG/DTA) for examining clay minerals in rocks are presented. These methods were used for determination of mineral composition in sedimentary rock samples from the shaft No.4 Frenštát -West, Northern Moravia, CZ.

Previously, the samples representing the basic clay mineral specimen were investigated by means of the following methods. In order to provide an adequate characterization of these samples, X-ray diffraction and X-ray fluorescence spectroscopy were utilized. As the individual clay minerals often occur in a form of mixed-layer clay minerals with various ratios of individual components, IR spectra and TG/DTA curves of mineral mixtures (either natural or synthetic) were recorded, too.

Clay minerals represented mainly by fine-crystalline illite (muscovite) with traces of kaolinite were predominant. Besides, carbonates (calcite, ankerite) and silica minerals occurred in these samples, too. A presence of pyrites and coal matter was confirmed only by thermal analysis. Traces of feldspars were detected by means of FTIR spectroscopy in some rock samples.

**KEYWORDS:** clay mineral, mixed-layer clay minerals, FTIR-spectroscopy, thermal analysis (TG/DTA)

**EFFECT OF SONICATION ON STRUCTURE  
AND PARTICLES DIVISION OF PYROPHYLLITES**

**Andrzej WIEWIÓRA <sup>1)</sup>, Jaromír DRAPALA <sup>1)</sup>, José Luis PÉREZ-RODRÍGUEZ <sup>1)</sup>, Luis Allan PÉREZ-MAQUEDA <sup>2)</sup> and Dorota GRABSKA <sup>1)</sup>**

<sup>1)</sup> *Institute of Geological Sciences, Polish Academy of Sciences, ul. Twarda 51/55, 00-818 Warsaw, Poland*

<sup>2)</sup> *Instituto de Ciencia de Materiales de Sevilla, Consejo Superior de Investigaciones Científicas - Universidad de Sevilla, c. Américo Vespucio, s/n. Isla de la Cartuja 41092 Sevilla, Spain*

*\*Corresponding author's e-mail: wiewiora@twarda.pan.pl*

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#### **Abstract**

Pyrophyllites from Zalamea (Badajoz, Spain) and from Hillsboro North Carolina USA), were subjected to treatment in ultrasonic liquid processor and studied by BET, SEM and XRD methods in an attempt to reveal changes in structure ordering and particle sizes. Original sample of pyrophyllite from Zalamea is characterized by clay size particles and well organised polytypic structure 1AA-II,1. During 5 hrs of sonication the structure suffered only small destruction, but further sonication for 10 hrs produced significant structure disorder marked by smearing out of all the polytypic 021, 111 reflections. Pyrophyllite from Hillsboro is represented by lath-crystals of macroscopic size, displaying poorly ordered structure classified to subfamily A of polytypes. MDO group and polytype could not be determined and stay unknown. Changes in particle sizes in terms of specific surface area, e.s.d. and best mean thickness of the domains of coherent X-ray scattering were most rapid during first 10 hrs of sonication, similar in the both studied pyrophyllites. Limit of particle division was achieved after 20 hrs – 40 hrs sonication. Irrespective of differences in the initial morphology and structural order the samples finally divided during sonication reached similar particle sizes (e.s.d. around 30 nm), best mean thickness of the domains of coherent scattering (around 12 nm) and show alike structural disorder.

**KEYWORDS:** pyrophyllite, polytypes, sonication