

ADVANCED ANALYTICAL TECHNIQUES FOR CLAY CHARACTERIZATION

Tuesday June 22, 2004

Advanced Analytical Techniques for Clay Characterization Poster Session	
5:00p	<p>POLYTYPE AND MORPHOLOGY ANALYSES OF KAOLIN MINERALS BY ELECTRON BACK-SCATTERING DIFFRACTION (EBSD). Toshihiro Kogure¹, and Atsuyuki Inoue²</p> <p>¹Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, ²Department of Earth Sciences, Faculty of Science, Chiba University</p>
	<p>IN-SITU XRD MEASUREMENTS OF INTERLAYER SWELLING OF CLAYS. Michael Plötze*, and Günter Kahr</p> <p>Environmental Engineering and Clay Mineralogy, Institute for Geotechnical Engineering, ETH Zurich, 8093 Zurich, Switzerland</p>
	<p>SOFT X-RAY SPECTROMICROSCOPY AND ATR-FTIR STUDY OF CLAY MINERAL-NATURAL ORGANIC MATTER SUSPENSIONS.</p> <p>Tae Hyun Yoon^{*1}, Karim Benzerara¹, Stephen B. Johnson¹, Tolek Tyliczszak², David Shuh², and Gordon E. Brown, Jr.^{1,3}</p> <p>¹Surface & Aqueous Geochemistry Group, Department of Geological & Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA; ²Lawrence Berkeley National Laboratory, Advanced Light Source, Berkeley, CA 94720 USA; ³Stanford Synchrotron Radiation Laboratory, SLAC, 2575 Sand Hill Road, Menlo Park, CA 94025, USA</p>

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Advanced Analytical Techniques for Clay Characterization I	
1:20 – 1:40p	<p>DIRECT DETERMINATION OF DEFECT STRUCTURES IN KAOLIN MINERALS BY HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM). Toshihiro Kogure^{*1}, and Atsuyuki Inoue²</p> <p>¹Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, ²Department of Earth Sciences, Faculty of Science, Chiba University</p>
1:40 – 2:00p	<p>CRYSTAL STRUCTURE OF BIRNESSITE: FROM WELL-CRYSTALLIZED TO HIGHLY-DEFECTIVE STRUCTURES. Anne-Claire Gaillot^{*1,2}, Bruno Lanson², Victor A. Drits^{2,3}, and Alain Manceau²</p> <p>¹Department of Earth & Planetary Sciences, Johns Hopkins University, Baltimore, MD 21218, USA; ²Environmental Geochemistry Group, LGIT - Maison des Géosciences, University of Grenoble-CNRS, 38041 Grenoble Cedex 9, France; ³Geological Institute, Russian Academy of Sciences, Moscow, Russia</p>
2:00 – 2:20p	<p>IN-SITU MONITORING OF SOLUTION-CLAY REACTIONS BY WET-CELL X-RAY DIFFRACTION (WC-XRD) TECHNIQUES.</p> <p>Laurence N. Warr</p> <p>Centre de Géochimie de la Surface (CNRS-ULP), 1 rue Blessig, 67084-Strasbourg, France</p>

2:20 – 2:40p	<p>QUANTITATIVE RIETVELD PHASE ANALYSIS OF SMECTITES USING A SINGLE LAYER APPROACH. Kristian Ufer¹, Reinhard Kleeberg*², and Jörg Bergmann³</p> <p>¹Rheinisch-Westfälische Technische Hochschule Aachen, Institut für Mineralogie und Lagerstättenlehre, Wüllnerstr. 2, D-52056 Aachen, Germany; ²Technische Universität Bergakademie Freiberg, Institut für Mineralogie, D-09596 Freiberg, Germany; ³Ludwig-Renn-Allee 14, D-01217 Dresden, Germany.</p>
2:40 – 3:00p	<p>OUTCOMES OF THE SECOND REYNOLDS CUP IN QUANTITATIVE MINERAL ANALYSIS OF CLAY BEARING SAMPLES. Reinhard Kleeberg</p> <p>Technische Universität Bergakademie Freiberg, Mineralogisches Institut, D-09596 Freiberg, Germany</p>
Advanced Analytical Techniques for Clay Characterization II	
3:20 – 3:40p	<p>ELECTRICAL CONDUCTIVITY SPECTRA OF SMECTITES AS INFLUENCED BY SATURATING CATION AND HUMIDITY. Sally D. Logsdon and David A. Laird*</p> <p>USDA, ARS, National Soil Tilth Laboratory, 2150 Pammel Dr., Ames, IA 50011</p>
3:40 – 4:00p	<p>SMECTITES FOR TAILORED APPLICATIONS. Felicitas Wolters¹, Gerhard Lagaly², Guenter Kahr³, and Katja Emmerich*⁴</p> <p>¹BGR, Stilleweg 2, 30655 Hannover, ²University Kiel, Institute of Inorganic Chemistry, 24098 Kiel, both Germany, ³ETH-IGT, Hoenggerberg, 8093 Zurich, Switzerland, ⁴FZK-ITC-WGT, PO Box 3640, 76021 Karlsruhe, Germany</p>
4:00 – 4:20p	<p>IRON-BEARING COMPOUNDS FORMED DURING AGING OF RESIDUES FROM INDUSTRIAL KAOLIN LEACHING: A VARIABLE TEMPERATURE MÖSSBAUER STUDY. *Fabiana R. Ribeiro^{1,3}, Wagner N. Mussel¹, José D. Fabris¹, Vijayendra K. Garg², Joseph W. Stucki³</p> <p>¹Department of Chemistry, Federal University of Minas Gerais, Belo Horizonte, MG 31270-901 Brazil; ²Institute of Physics, University of Brasilia, Brasília, DF 70919-970, Brazil; ³Department of Natural Resources and Environmental Sciences, University of Illinois, Urbana, IL 61801 USA; *fribeiro@uiuc.edu</p>

TUESDAY JUNE 22, 2004

ADVANCED ANALYTICAL TECHNIQUES FOR CLAY CHARACTERIZATION

POSTER SESSION

5:00PM

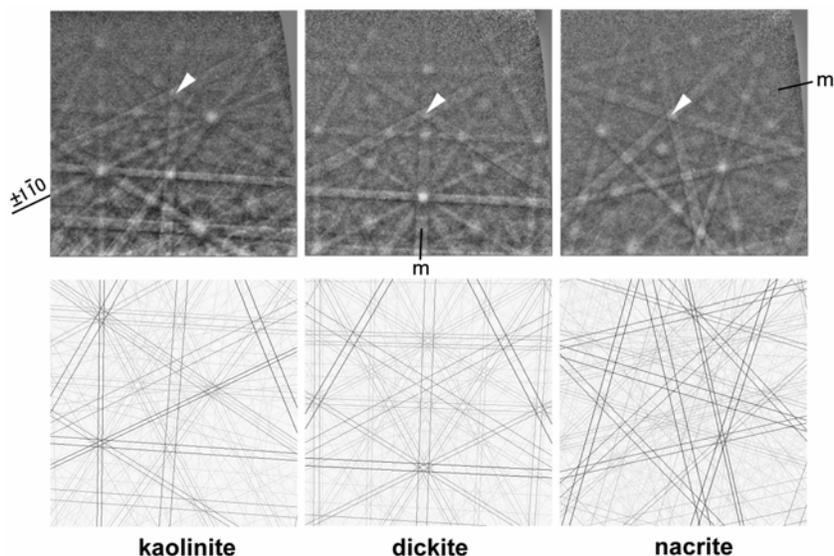
POLYTYPE AND MORPHOLOGY ANALYSES OF KAOLIN MINERALS BY ELECTRON BACK-SCATTERING DIFFRACTION (EBSD)

Toshihiro Kogure¹, and Atsuyuki Inoue²

¹Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, ²Department of Earth Sciences, Faculty of Science, Chiba University

Electron back-scattering diffraction (EBSD) technique has been applied to fine-grained kaolin minerals to determine the polytypes (kaolinite, dickite and nacrite) for individual grains and their crystal orientations in a scanning electron microscope (SEM). Kaolin particles dispersed on a flat substrate and carbon-coated were prepared for the EBSD analyses. Because kaolin minerals are prone to radiation damage by intense electron beam that is necessary to obtain EBSD patterns, the beam during pattern acquisition should be radiated on a certain specimen area with scanning mode. Kaolinite-dickite or nacrite are easily distinguished by trigonal or hexagonal symmetries around the $[001]^*$ direction respectively, of the Kikuchi bands corresponding to family reflections. Ordered dickite can be differentiated from kaolinite with a mirror plane passing the $[001]^*$ direction and characteristic Kikuchi poles.

As EBSD analysis is performed in a SEM, morphological characters can be corresponded to polytypes. Oriented overgrowth of dickite fragments on nacrite plates was found on a sample of hydrothermal origin. Ordered dickite always has euhedral shapes in a diagenetic kaolinite-dickite mixture specimen. Combination of EBSD and SEM observation enables morphology analysis for fine crystals as clay minerals. Lath-shaped diagenetic dickite is definitely elongated along the a -axis directions. Rhombohedral dickite consists of crystal planes with indices of $\{-111\}$ as side-facets.



(Top) EBSD patterns from kaolinite, dickite and nacrite. (Bottom) Calculated Kikuchi patterns in the same orientation. The position corresponding to the $[001]^*$ direction is indicated with the arrowhead in each pattern.

IN-SITU XRD MEASUREMENTS OF INTERLAYER SWELLING OF CLAYS

Michael Plötze*, and Günter Kahr

Environmental Engineering and Clay Mineralogy, Institute for Geotechnical Engineering, ETH Zurich, 8093 Zurich, Switzerland

The swelling phenomenon of clays is one of the most important topics in the engineering and environmental work. Swelling is a time dependent volume increase involving physicochemical reactions with water. There are two categories of swelling. The inner and intracrystalline swelling is a process whereby the exchangeable cations in the interlayer and at the surface of clay minerals build one to four discrete hydration shells. At higher water content, the formation of non solvated (non bound) water is observed. The osmotic (intracrystalline) swelling results from the difference in the ion concentrations close to the clay mineral surfaces and in the pore water.

The ionic composition influences the extent of swelling, due to the different hydration energies of the cations, which depends from ionic size and valence. Furthermore the swelling behaviour of clayey soils and rocks depends strongly on the mineralogical composition, i.e. on the type and quantity of clay minerals encountered and on the content of further minerals which show swelling behaviour caused by recrystallisation processes. The fabric and density of clays determines the time dependent swelling behaviour. Understanding the effects of cation valence, cation hydration energy and clay layer charge provides a model to calculate the swelling pressure.

Combined experimental studies were carried out on bentonite (MX80 Wyoming and Montigel Sudchemie) as a model clay: isothermic water adsorption measurements in a gravimetric apparatus of McBain type, swelling pressure measurements in an adapted oedometer apparatus, and interlayer swelling studies with XRD at various relative humidity.

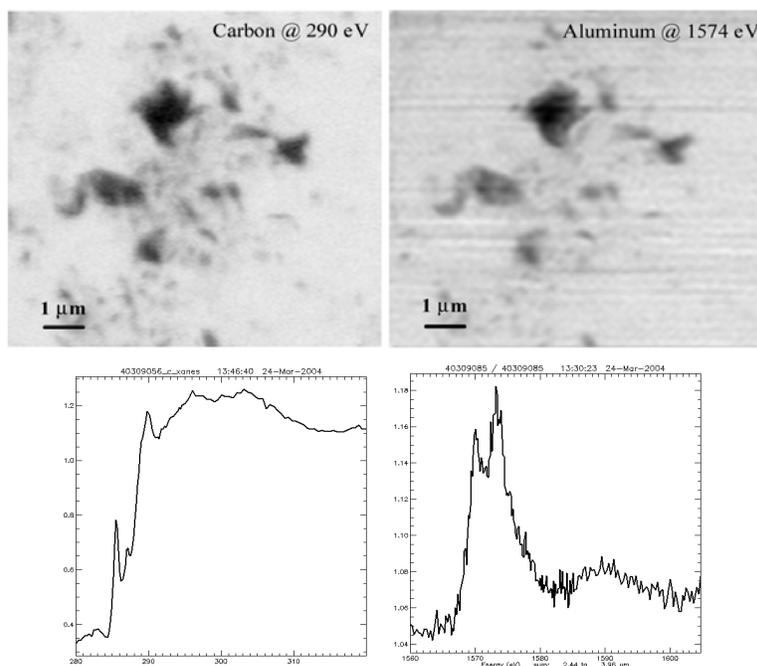
Results of in-situ XRD studies of interlayer swelling $d(001)$ will be presented for homoionic montmorillonite. The montmorillonite were exchanged with Cs^+ , Na^+ , Sr^{2+} , Ca^{2+} , Al^{3+} (related enthalpy of hydration from 276 to 4665 kJ/mol). The measurements were performed in a sample chamber (Anton Paar TTK450) mounted on a Bruker AXS D8. The relative humidity (RH) was achieved by mixing wet and dry pressure air at 26°C (Sycos H). The sample temperature (26.0 ± 0.2°C) was controlled by circulating water in the double chamber wall and the sample stage. Firstly the oriented samples were dried in vacuum oven (12h at 65°C). After that the XRD measurements were carried out in programmed cycles in the RH range 1-80 ± 0.2% (stabilization and equilibration time of RH within 60 min).

SOFT X-RAY SPECTROMICROSCOPY AND ATR-FTIR STUDY OF CLAY MINERAL-NATURAL ORGANIC MATTER SUSPENSIONS

Tae Hyun Yoon^{*1}, Karim Benzerara¹, Stephen B. Johnson¹, Tolek Tyliczszak², David Shuh², and Gordon E. Brown, Jr.^{1,3}

¹Surface & Aqueous Geochemistry Group, Department of Geological & Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA; ²Lawrence Berkeley National Laboratory, Advanced Light Source, Berkeley, CA 94720 USA; ³Stanford Synchrotron Radiation Laboratory, SLAC, 2575 Sand Hill Road, Menlo Park, CA 94025, USA

Colloid-facilitated transport of contaminants has been suggested as one of the primary transport mechanisms in subsurface waters. Moreover, interactions between colloid components (e.g., clay minerals, humic acids, and bacteria) are thought to play an important role in determining colloid stability and the transport of adsorbed pollutant species. In this study, we have combined soft x-ray spectromicroscopic methods and ATR-FTIR spectroscopy to investigate interactions between natural colloid components such as clay minerals and Suwannee river humic acid. STXM (scanning transmission x-ray microscopy) and XANES (x-ray absorption near edge structure) measurements have been performed on these systems under *in-situ* condition at the Advanced Light Source on the new Molecular Environmental Science beamline 11.0.2. Using STXM image stacks obtained at both the Al K- and C K-edges, we can identify nm-sized clay mineral particles associated with humic acid under hydrous conditions. Additionally, ATR-FTIR spectroscopic measurements were also conducted to investigate molecular-level interactions between these components under various pH and concentration ratio conditions. These FTIR results will also be discussed.



C K-edge (left) and Al K-edge (right) STXM Images and XANES Spectra of Montmorillonite (sAz) + Suwannee River Humic Acid Mixtures at pH =2.5

WEDNESDAY JUNE 23, 2004

ADVANCED ANALYTICAL TECHNIQUES FOR CLAY CHARACTERIZATION I

1:20PM

DIRECT DETERMINATION OF DEFECT STRUCTURES IN KAOLIN MINERALS BY HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM)

Toshihiro Kogure^{*1}, and Atsuyuki Inoue²

¹Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, ²Department of Earth Sciences, Faculty of Science, Chiba University

Near-atomic resolution TEM imaging (Fig. 1) has been successfully applied to determine the stacking defect structures in kaolin minerals, especially in kaolinite. The specimen studied is at mid-stage of the depth-related kaolinite-to-dickite transformation in a sandstone reservoir. Although electron radiation damage is a serious obstacle, a number of high-quality images were recorded on films, in which the tetrahedral and octahedral positions in a kaolinite unit layer were clearly resolved. Electron diffraction and high-resolution imaging of dickite showed that few stacking defects exist in this polytype. On the other hand, kaolinite crystals contain high density of stacking defects. These defects or stacking disorder are formed by mixture of the two kinds of lateral interlayer shifts, t_1 (approximately $-a/3$) and t_2 ($-a/3 + b/3$), between adjacent layers (Fig. 2). Disorder by the coexistence of B layer and C layer, or dickite-like stacking sequence was never observed. These results provide not only an unambiguous settlement for the long controversy of the defect structures in kaolinite, but also a new clue to understand kaolinite-to-dickite transformation mechanism.

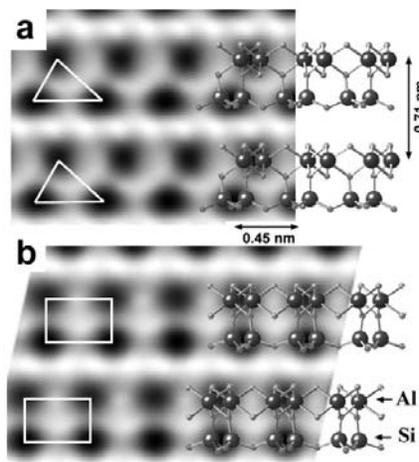


Fig. 1. Crystal structure and corresponding multi-slice simulated image of kaolinite, viewed down (a) [100] and (b) [110]. In the crystal structure model, Al and Si atoms are represented as large spheres and oxygen (hydroxyl) atoms as small spheres.

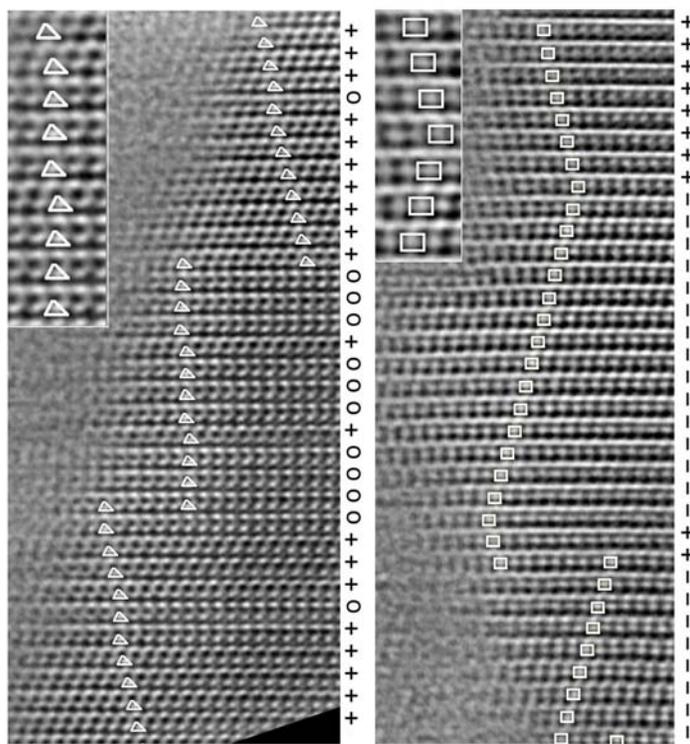


Fig. 2. Two filtered HRTEM images of disordered kaolinite. The marks of “o”, “+” and “-” at the right of the figures indicate no-, left- and right-hand staggers respectively, from the under layer. The insets at the top-right are the magnified images of portions in the lower-magnified ones.

CRYSTAL STRUCTURE OF BIRNESSITE: FROM WELL-CRYSTALLIZED TO HIGHLY-DEFECTIVE STRUCTURES

Anne-Claire Gaillot^{*1,2}, Bruno Lanson², Victor A. Drits^{2,3}, and Alain Manceau²

¹Department of Earth & Planetary Sciences, Johns Hopkins University, Baltimore, MD 21218, USA; ²Environmental Geochemistry Group, LGIT - Maison des Géosciences, University of Grenoble-CNRS, 38041 Grenoble Cedex 9, France; ³Geological Institute, Russian Academy of Sciences, Moscow, Russia.

Birnessite is a manganese oxide containing predominantly Mn⁴⁺ cations in layers of edge-sharing octahedra. Layer charge deficit arises from the presence of Mn³⁺ and/or vacant octahedra within layers and is compensated for by the presence of interlayer cations.

Despite the relatively low abundance of manganese, birnessite is ubiquitous in nature and is essential to the geochemistry of soils and oceanic nodules because of its remarkable cation exchange capacity, sorption, and redox properties. In particular, because of its high affinity for pollutants (heavy metals, organics, ...) this mineral plays a pivotal role in their fate in contaminated environments.

This layered Mn oxide, that can be synthesized using various chemical routes, presents a high structural variability depending on the physico-chemical conditions of formation. The coupling of several characterization techniques, such as X-ray diffraction (monocrystal, or powder), X-ray absorption spectroscopy and electron diffraction, is often necessary to access structural details fundamental to understanding the reactivity for each variety. In particular, such coupling allows solving the structure of the layers and determining the origin of their charge. In addition, the stacking mode of the birnessite layers determines the structure of the interlayer region and the configuration of the sites available for cation adsorption.

Birnessite also exhibits random or well-defined stacking faults that are common in layered structures. The high proportion of such structural defects strongly reduces the efficiency of usual structure refinement methods, including the Rietveld method. One of the most effective ways to determine the actual structure of these defective systems is the calculation of XRD patterns using the mathematical formalism described in detail by Drits and Tchoubar (1990). This trial-and-error procedure allows determining, in addition to the structural information obtained for well-ordered birnessite varieties, the nature, abundance and distribution of the defects.

Even in the most defective structures, when the abundance of random stacking faults leads to the occurrence of extremely disordered structures without three-dimensional ordering (turbostratic stacking), X-ray diffractograms of birnessite exhibit noticeable modulations and relevant structural information, which includes not only unit-cell parameters but also the atomic coordinates and occupancies of the different sites, can be obtained.

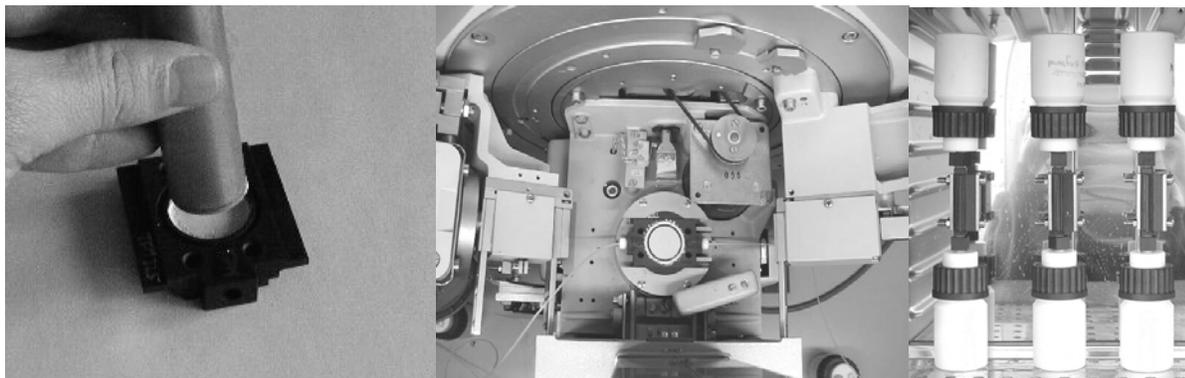
Drits and Tchoubar (1990), X-ray Diffraction by Disordered Lamellar Structures. *Springer-Verlag*

IN-SITU MONITORING OF SOLUTION–CLAY REACTIONS BY WET-CELL X-RAY DIFFRACTION (WC-XRD) TECHNIQUES

Laurence N. Warr

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A flow-through reaction cell (wet-cell) has been developed for the routine investigation of solution – fine powder reactions by X-ray diffraction analysis (Warr and Hofmann, 2003). This device is ideal for studying both short-term hydration, and long-term alteration reactions of clays in solution. In this contribution some examples will be presented from the hydration of Ca- and Na-montmorillonite in natural solutions (ground- and sea-waters), and from the hydrothermal alteration (85°C) of Mesozoic repository shales under the influence of strongly alkaline solutions produced by alteration of concrete. The wet-cell device is considered to be a new and useful tool for investigating clay applications in the disposal of nuclear waste material, as well as many other geoscientific problems.



Wet-cell X-ray diffraction techniques used to monitor solution-clay reactions of compacted powders. *Left*: Pressing of a bentonite powder into the wet-cell device. *Middle*: In-situ X-ray diffraction measurement of the wet-cell experiment with teflon hoses attached. *Right*: Percolation of solutions through the sealed wet-cell device at 85°C in an air-oven.

Reference

Warr, L.N. and Hofmann, H. (2003). In-situ monitoring of powder reactions in percolating solution by wet-cell X-ray diffraction techniques. *Journal of Applied Crystallography*, 36, 948-949.

QUANTITATIVE RIETVELD PHASE ANALYSIS OF SMECTITES USING A SINGLE LAYER APPROACH

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¹Rheinisch-Westfälische Technische Hochschule Aachen, Institut für Mineralogie und Lagerstättenlehre, Wüllnerstr. 2, D-52056 Aachen, Germany; ²Technische Universität Bergakademie Freiberg, Institut für Mineralogie, D-09596 Freiberg, Germany; ³Ludwig-Renn-Allee 14, D-01217 Dresden, Germany

The quantification of clay minerals is a frequent task in geosciences, engineering and oil industry. Among the XRD techniques, the Rietveld method is widely accepted to be a suitable tool for quantitative phase analysis (QPA). Very precise results can be obtained for materials containing well ordered phases like cement clinker, ceramics and some types of rock samples. Because the Rietveld method uses discrete Bragg peaks, it is apparently unable to calculate diffraction patterns of strongly disordered layer structures. The smectite group represents an excellent example of extreme disorder in layer stacking, the so-called turbostratic disorder. For such materials, the sharp *hkl* spots in reciprocal space smear to continuous *hk* rods in c^* direction. A way to approximate these rods by series of spots is the construction of a cell that is elongated in c^* , filled only by one layer at the bottom. This approach results in *hkl* reflection series with unusual high *l* that sum up the well-known asymmetric *hk* bands of turbostratically disordered materials. The resulting unrealistic *00l* series must be sorted for “true” reflections (with $l = n$ times the elongation factor) to reproduce the rational basal series. Additional line broadening parameters have to be introduced for the *00l* to correctly approximate the thickness of the stacks as well as for the *hkl* to approximate the diameter of the *hk* rods. Scale factors must be corrected for the partial filling of the cell. Such formulations can be done with the help of the structure interpreter language in the BGMN Rietveld program. We used the atomic positions of Tsipursky & Drits (1984) for the dioctahedral 2:1 layers and a cation-water complex in the interlayer space in a ten times elongated cell to calculate the diffraction pattern of montmorillonite. In a first trial, the mean chemical composition was taken from chemical analysis of a $< 0.2 \mu\text{m}$ fraction of a white bentonite. The powder pattern of this material could be modeled very well. In order to check the reliability of this approach for QPA, mixtures of montmorillonite, kaolinite, illite and quartz have been prepared. Standard powder patterns were collected and analyzed. Lattice parameters for all phases, some occupation factors, complicated *hkl* dependent broadening of the kaolinite, preferred orientation parameters as well as a 5th degree background polynomial, sample displacement and zero point parameters, all together 56 to 73 parameters, were refined automatically without any user intervention. The results are encouraging: All concentrations could be reproduced to not more than ± 3 wt-% difference from the correct values. We obtained only moderate complementary deviations of the montmorillonite and illite concentrations from their actual values, possibly caused by the insufficient description of the disordering features of the illite component. The calculation time required for a single cycle is in the magnitude of a few seconds. Routine powder patterns of real sedimentary samples, containing up to 10 detectable minerals, could be analyzed by refining of 87 parameters in about 10 minutes using a 2 GHz personal computer. In further work, the model will be adapted to trioctahedral smectites. Additionally, the chance to refine reliable occupation factors of the octahedral and of the interlayer positions will be checked out.

OUTCOMES OF THE SECOND REYNOLDS CUP IN QUANTITATIVE MINERAL ANALYSIS OF CLAY BEARING SAMPLES

Reinhard Kleeberg

Technische Universität Bergakademie Freiberg, Mineralogisches Institut, D-09596 Freiberg, Germany

The first Reynolds Cup was initiated by colleagues from ChevronTexaco and the U.S. Geological Survey to stimulate the development of methods for quantitative mineral analysis of clay-bearing rocks (McCarty, 2002). After the results of the contest have been published at the 2002 CMS meeting in Boulder(CO), an “ad hoc” committee decided to continue with a second contest in 2004. This one is supported by the Deutsche Forschungsgemeinschaft (German Research Council), the Clay Minerals Society, the German-Swiss-Austrian Clay Group (DTTG) and the Commission on Powder Diffraction of the International Union of Crystallography. The second Reynolds Cup was announced at some mineralogical and crystallographical conferences in 2003 as well as at the DTTG homepage and to the CMS, MSA and IUCr Rietveld listservers in December 2003. The 60 sets each containing 3 mineral mixtures have been requested by the interested people in about 4 days after sending the start signal to the listservers. This indicates the great interest of the community in improving the analytical methods. The samples have been sent out to these 60 laboratories in 18 countries of 5 continents during the late December 2003. The only information given to the participants was that the compositions were designed to represent three different types of sedimentary rocks (mudstone, sandstone, saliniferous rock). The mixtures were prepared from pure mineral samples, obtained mainly from the collections of the Technical University Bergakademie Freiberg/Germany. Clean minerals were hand-picked from broken single crystals or separated by chemical treatment and size fractionation in the case of clay minerals. These reference minerals have been screened for purity by XRD and other techniques. All materials were broken to < 0.4 mm size for main components and to < 0.2 mm or < 0.1 mm for minor components of the planned mixtures. The air-dried material was weighted in for a total mass of 256 g of each mixture. These samples were homogenized by one day overhead tumbling in 800 ml glass bottles together with mixing balls. Then, the mixtures were split into 8 parts in an rotary sample splitter and recombined 5 times. After a further splitting run, the 8 splits were split again into 8 parts (now 4 g) using a micro-rotary splitter. In this way 64 4-g-units of each mixture were obtained. In order to check the homogeneity of the splits, 3 sample sets were taken randomly from these 64 units. Two of them were divided into two parts used for XRD and XRF analysis, respectively. The third sample was quartered to check the chance to take representative 1 g sub-samples also from a single sample set. Two of these quarters were also ground in a McCrone micronizing mill and XRD patterns were measured. No significant differences could be seen in the XRD patterns and in the XRF results for all these sub-samples. The participants had about four months (until May 1st) to carry out their analyses. All methods for phase identification and quantification were allowed. To avoid nomenclature problems during reporting and judging the results, some grouping of minerals was done in the same way as in the first contest. Again we used simply the sum of deviations from actual wt-% (“bias”) as a criterion for the quality of the analyses. Details of the results are presented in this talk. The winner of the 2004 Reynolds cup is ... the whole clay community ☺!

WEDNESDAY JUNE 23, 2004

ADVANCED ANALYTICAL TECHNIQUES FOR CLAY CHARACTERIZATION II

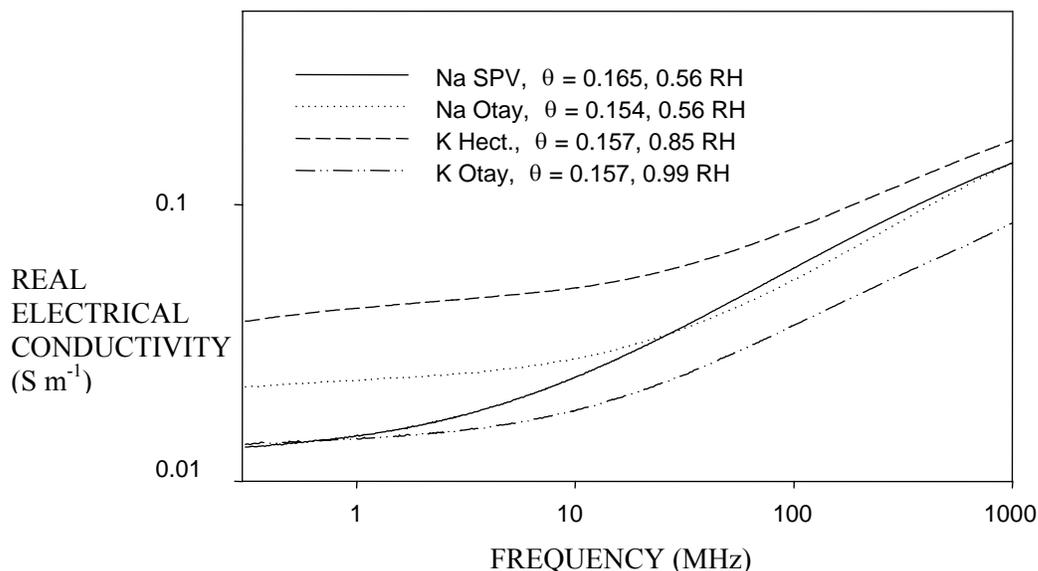
3:20PM

ELECTRICAL CONDUCTIVITY SPECTRA OF SMECTITES AS INFLUENCED BY SATURATING CATION AND HUMIDITY

Sally D. Logsdon and David A. Laird*

USDA, ARS, National Soil Tilth Laboratory, 2150 Pammel Dr., Ames, IA 50011

Electrical conductivity is an important soil property related to salinity, and is often used for delineating other soil properties. The purpose of this study was to examine the influence of smectite properties on the complex electrical conductivity spectra of hydrated smectites. Four reference smectites were saturated with Ca, Mg, Na, or K and equilibrated at four relative humidities (RH) ranging from 56 to 99%. X-ray diffraction was used to determine fractions of the various smectite layer hydrates (0 to 4 layers of interlayer water molecules) in each sample. A vector network analyzer was used to determine the real component of the complex electrical conductivity spectra (σ') for frequencies (f) ranging from 300 kHz to 3 GHz. Values of the d.c. electrical conductivity (σ_0), the frequency where the slope changes in the spectra (f_r), and the slope at the high frequency end of the spectra (n) were determined by fitting σ' to $\sigma'(f) = \sigma_0(1 + f / f_r)^n$. Both σ_0 and f_r increased with the total amount of water, the amount of interlayer water, and for saturating cations in the following order; K<Mg <Ca<Na. The opposite trends were observed for n . Values of these parameters were influenced by the type of smectite, but the trends were not consistent for the effect of layer charge. The results indicate that interlayer water in smectites contributes to the electrical conductivity of hydrated smectites, and that polarization of water by local electrical fields has a substantial influence on the complex electrical conductivity spectra of smectites. The accuracy of salinity estimates for soils and sediments that are based on conductivity measurements may be adversely affected unless the effects of hydrated clays on electrical conductivity are considered. Example conductivity spectra are shown below.



SMECTITES FOR TAILORED APPLICATIONS

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Nanosized synthetic particles are a main focus in nanotechnology. Already natural nanoparticles, such as clay minerals are frequently used in nanocomposites. Many of these applications are not aware of the great variety clay minerals possess in structure and properties. Hence, the full potential of these particles for low-cost nanofillers is not regarded.

A comprehensive classification is necessary to take advantage of structural features offered by different 2:1 layer structures and to tailor nanofillers.

Until now classifications (Grim and Kulbicki, 1961, Schultz, 1969, Brigatti, 1983) disregarded the dehydroxylation behavior, which means that the structure of the octahedral layer of smectites remained unconsidered. Although the cis- and trans-vacant character of dioctahedral smectites is known for a long time a manageable method to determine this property was lacking for smectites until recently because of their turbostratic disorder. Drits et al. (1995) showed that the dehydroxylation temperature of all dioctahedral 2:1 clay minerals is related to the structure of the octahedral sheet. Trans-vacant minerals dehydroxylate at 500°C and cis-vacant varieties at 700°C. Mixed types also exist which show two dehydroxylation peaks.

Within the types of the common classification systems there are smectites which can not be assigned to any type of the nomenclature. Therefore, we propose to combine a systematic description and trivial names. The systematic name should describe layer charge, octahedral structure, tetrahedral charge, Fe-content and type of mineral like “high charged cis-vacant beidellitic _ montmorillonite” taking into account rules of IMA and AIPEA to characterize montmorillonites definitely. Trivial names like “Cheto-type montmorillonite” taking into account common classification systems as mentioned above can be used if their octahedral cation distribution allow this. Various data of smectites were collected from literature and the evaluation of our system was started. However, in many cases, data sets from literature do not provide all required information. Therefore, a series of 32 samples is under examination. First results indicate a relation between iron content, location of charge and dehydroxylation temperature. Cross checks like K⁺- and Li⁺-test will serve as additional tools for characterization.

Brigatti (1983) *Clay Minerals*, 18, 177-186.

Drits, Besson and Muller (1995) *Clays and Clay Minerals*, 43, 718-731.

Grim and Kulbicki (1961) *The American Mineralogist*, 46, 1329-1369.

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IRON-BEARING COMPOUNDS FORMED DURING AGING OF RESIDUES FROM INDUSTRIAL KAOLIN LEACHING: A VARIABLE TEMPERATURE MÖSSBAUER STUDY

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The industrial beneficiation of kaolin involves removal of iron (oxyhydr)oxides and other impurities that impart unwanted colors to the kaolin, which depreciate its commercial value, particularly to the paper industry. While the beneficiation process creates a better kaolin product, it also yields a waste residue for which environmentally proper and commercially viable disposition has proven difficult. The chemical leaching process often requires the addition of metallic zinc and sulfuric and phosphoric acids, causing the leachate to be highly acidic and hazardous to the environment. In order to render the residue less harmful, the industry instituted a neutralization step in which calcium oxide is added. The residue is then transferred to an open pond and allowed to evaporate. During this step the Fe also reprecipitates. As the pond evaporates, the dry residue accumulates and the Fe oxides begin to age and transform to more stable Fe-rich compounds. Stockpiles of these residues are increasing and methods for disposing of rather than just storing them is becoming increasingly important. In order to accomplish this goal, a better understanding of the properties and behavior of the residue is needed.

The purpose of this study was to identify the Fe oxides that are present in the residues and characterize their transformations during aging. Kaolin reject materials from an industrial plant in Brazil were studied by ⁵⁷Fe Mössbauer spectroscopy, including samples from residues aged for different periods of time. The kinetics of the Fe reactions are relatively slow and the most stable Fe oxides can only be accurately detected after a long aging time. Although data obtained with powder x-ray diffractometry, thermogravimetry, and scanning electron microscopy provided indispensable information about the crystal structure and morphology of these materials, Mössbauer spectroscopy proved to be an especially powerful technique to identify and help trace the inter-conversion mechanisms of the Fe-bearing species. In some samples, differential chemical dissolution was performed prior to Mössbauer analysis in order to distinguish between well-crystallized and poorly crystallized Fe oxide forms, enabling a more precise characterization of the Fe compounds. Mössbauer data handling with quadrupole splitting distribution was also utilized to enhance identification of the hydr(oxides) in the residue samples. At the initial aging step of the residue, the only (oxyhydr)oxides were lepidocrocite and akaganeite. Goethite and hematite were the main Fe-rich compounds found in the most aged residue.