MAGNETIC RESONANCE SPECTROSCOPY OF CLAYS I

Wednesday June 23, 2004

Magnetic Resonance Spectroscopy of Clays I	
9:00 – 9:40a	**SOME APPLICATIONS OF EPR SPECTROSCOPY TO MINERALS, FOR THE NON-EXPERT.** John A. Weil Saskatchewan Solid-State EPR Centre, Dept. of Chemistry (& Geosciences), Univ. of Saskatchewan, 110 Science Pl., Saskatoon, SK, S7N 5C9, Canada
9:40 – 10:00a	**EPR STUDIES OF COPPER EXCHANGED SMECTITE AND THE BEHAVIOUR UPON HEATING.** Michael Plötze[*1], and Katja Emmerich[2] [1]Environmental Engineering and Clay Mineralogy, Institute for Geotechnical Engineering, ETH Zurich, 8093 Zurich, Switzerland; [2]Institute for Technical Chemistry, Forschungszentrum Karlsruhe GmbH, 76021 Karlsruhe, Germany
Magnetic Resonance Spectroscopy of Clays II	
10:20 – 11:00a	**NMR CHARACTERIZATION OF THE STRUCTURE AND DYNAMICS IN MODIFIED CLAYS AND POLYMER/CLAY NANOCOMPOSITES.** J. Grandjean University of Liege, Department of Chemistry B6a, COSM, B-4000 Liege, Belgium
11:00 – 11:40	**SOLID-STATE NMR STUDIES OF THE TRANSFORMATION OF CLAY MINERALS IN THE ENVIRONMENT.** Karl T. Mueller[*1], Garry S. Crosson[1], Geoffrey M. Bowers[1], Jon Chorover[2], and Sunkyung Choi[2] [1]Penn State University, Department of Chemistry, 104 Chemistry Building, University Park, PA, 16802; [2]University of Arizona, Department of Soil, Water and Environmental Science, Tucson, AZ, 85721
11:40 – 12:00p	**NANOSTRUCTURATION OF PYRIDINE GUEST MOLECULES ENTRAPPED IN THE TUNNELS OF SEPIOLITE.** Wenxing Kuang[*], Glenn A. Facey, and Christian Detellier Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

WEDNESDAY JUNE 23, 2004

MAGNETIC RESONANCE SPECTROSCOPY OF CLAYS I

9:00AM

SOME APPLICATIONS OF EPR SPECTROSCOPY TO MINERALS, FOR THE NON-EXPERT

John A. Weil

Saskatchewan Solid-State EPR Centre, Dept. of Chemistry (& Geosciences), Univ. of Saskatchewan, 110 Science Pl., Saskatoon, SK, S7N 5C9, Canada

I intend here to introduce the audience to the utility of electron paramagnetic resonance (EPR) spectroscopy in mineralogy, in particular to the art and science of extracting information from powdered samples. The audience will remember that EPR requires the presence of species with one or more unpaired electrons. The technique is extremely sensitive, dependent on the spectral linewidths at hand, capable of detecting down to 10^{-9} molar concentrations of such electrons. Variables include the sample temperature (T = 1 to 800 K), and the microwave frequency applied (ν = 1000 and these days up to ca. 500,000 MHz).

There are well over a 100 magnetic point defects in alpha-quartz now known and characterized. After their complex single-crystal EPR spectra are measured and analyzed, these data can be transformed by computer simulation to predict powder spectra. A library of such spectra, for various T and ν, is being produced and made available, and will enable quick identification of impurity and defect species in any samples containing quartz particles. Some special spectra, e.g., involving Ge(3+), Ti(3+) and Fe(3+), will be illustrated in this talk.

Attention will be paid to the complex art of determining from EPR the nature and local electrical symmetry of magnetic defects, and will be illustrated using our results on Gd(3+) in fluorapatite. In addition, the EPR characteristics of Mn(2+), as quantitatively measured by us, will be cited as offering a fine standard for comparison with other clays.

EPR STUDIES OF COPPER EXCHANGED SMECTITE AND THE BEHAVIOUR UPON HEATING

Michael Plötze[*1], and Katja Emmerich[2]

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Movement of small cations (e.g. Li^+, Cu^{2+}) from the interlayer into the 2:1 layer of montmorillonite upon heating is a well-known phenomenon (Hofmann & Klemen 1950, Heller-Kallai & Moser 1995). However, the position of the cations after migration is not yet clarified. EPR spectroscopy is helpful in monitoring the hydration state and the location of exchangeable d-ions (e.g. McBride & Mortland 1974, Mosser et al. 1997, McBride 1982, Karakassides et al. 1999, Emmerich et al. 2001). The aim of the present work is to improve the knowledge of interaction mechanisms of montmorillonite with heavy metal cations under wet conditions at temperatures up to 100°C, the fixing of heavy metals in the crystal structure of montmorillonite and its effects on the clay characteristics.

Homoionic Cu^{2+}-exchanged samples were prepared by washing the <2 µm fraction of bentonite from Linden (Bavaria) with a chloride solution (Emmerich et al. 1999). Air dry samples or suspension with mass content of 10% of these clays were altered in a water steam atmosphere in stainless steel autoclaves at 55 or 90°C up to six month. Samples were characterized by XRD and EPR. Electron Spin Resonance spectra of randomly oriented powder samples of Cu^{2+}-rich montmorillonite were recorded with a X-Band ESR-spectrometer (Bruker ESP 300E) at room temperature after allowing samples to soak humidity in an atmosphere of 75% relative humidity.

EPR spectra of Cu^{2+}-rich montmorillonite showed two peaks at g = 2.15 and 2.05 which are characteristic for $[Cu(H_2O)_6]^{2+}$ and $[Cu(H_2O)_4]^{2+}$, respectively, on interlayer positions. The intensity ratio of both peaks moved in favour of the signal at 2.15 after short time alteration (seven days), whereas the peak at 2.05 regained intensity after six months. Dry and suspension samples that were altered in a steam atmosphere at 90°C as well as at 55°C showed a similar behaviour.

EPR spectra show that the amount of fully hydratable Cu^{2+}-ions on interlayer positions depends on increasing time of treatment at lower temperatures. The reduction of concentration of $[Cu(H_2O)_6]^{2+}$ at interlayer positions is a reversible process at lower temperatures. The Cu^{2+}-cations are fixed by occupying hexagonal cavities of the tetrahedral sheet (Karakassides et al. 1999) and not strongly in previously vacant sites in the octahedral sheet (Mosser et al. 1997).

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MONDAY JUNE 23, 2004

MAGNETIC RESONANCE SPECTROSCOPY OF CLAYS II

10:20AM

NMR CHARACTERIZATION OF THE STRUCTURE AND DYNAMICS IN MODIFIED CLAYS AND POLYMER/CLAY NANOCOMPOSITES

J. Grandjean

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To obtain clay-polymer nanocomposites, one of the critical steps is the surface treatment of the mineral. Surfactants are usually ion-exchanged with interlamellar cations of the negatively charged mineral, ensuring its dispersion within the polymer matrix. The interaction between a typical organic cation and the mineral surface should be modulated by the location of cation isomorphous substitution and the charge density of the clay. Accordingly, we have used Laponite, a commercial synthetic hectorite, and synthetic saponites of variable interlayer charge. These minerals have been characterized by ^{27}Al, ^{29}Si MAS and ^{23}Na 2D 3QMAS NMR (1). The properties of the organically-modified clays are currently described by macroscopic techniques. We have used NMR spectroscopy in the solid-state to probe the structure, conformation and dynamics of the intercalated species.

After intercalation in Laponite, the properties of hexadecyltrimethylammonium ions are drastically changed compared to those of the pure organic salt. The ^{13}C CP MAS NMR spectrum of the hybrid compound indicates conformational flexibility of the surfactant hydrocarbon chain and the ^{13}C longitudinal relaxation times show high mobility of the alkyl chain (2). Then, we have extended this study to a few surfactants intercalated in Laponite and synthetic saponites, showing how chain dynamics are perturbed. The charge density modulates the trans/gauche conformational ratio of the surfactant alkyl chain, providing a deeper understanding of the variation of the basal spacings from X-ray diffraction (3). This ratio depends also on the location of cation isomorphous substitution in the clay. We have extended these studies to nanocomposites formed by poly(ε-caprolactone) and these modified clays.

Natural clays such montmorillonites are paramagnetic materials that prevent dynamic information from NMR relaxation data. However, the proton relaxation rate in the laboratory frame can be useful to characterize the montmorillonite dispersion within the polymer matrix (4), as proposed recently in the literature.

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SOLID-STATE NMR STUDIES OF THE TRANSFORMATION OF CLAY MINERALS IN THE ENVIRONMENT

Karl T. Mueller[*1], Garry S. Crosson[1], Geoffrey M. Bowers[1], Jon Chorover[2], and Sunkyung Choi[2]

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Environmental mobilities of radionuclides (such as ^{137}Cs and ^{90}Sr) are governed by their interactions with natural soil particles in the saturated and unsaturated zones at Department of Energy waste sites (*e.g.* the Hanford Site). High surface area aluminosilicate clay minerals are a component of the natural soils beneath the leaking waste tanks at these sites, and serve as possible radionuclide sorbents. However, due to the characteristics of the contaminant medium (high pH, high Al, and high ionic strength), clay minerals are susceptible to transformations during exposure to tank waste leachates. To gain a better understanding of fundamental processes taking place in the vadose and saturated soil environments in these affected areas, we are currently studying the transformation of clays under specific chemical conditions that mimic the composition of contaminant solutions.

In a first set of studies, specimen clay samples are reacted for varying time periods (up to one year) with simulated tank waste leachate (STWL) solutions containing fixed concentrations of (nonradioactive) Cs and Sr co-contaminants (at levels of 10^{-3}, 10^{-4}, and 10^{-5} M). Mineral dissolution and transformation are followed with solution analysis, x-ray diffraction, solid-state nuclear magnetic resonance (NMR), and a number of other analytic methods. We report here results from ^{27}Al magic-angle spinning (MAS) NMR, ^{29}Si MAS NMR, and ^{1}H/^{29}Si cross-polarization MAS (CPMAS) NMR, and we evaluate these results along with those of other parallel analytic studies. A number of neophases are identified through these analyses, and the use of solid-state NMR at multiple fields allows for superior resolution of resonances from different species. Ultimately, solid-state NMR results offer a powerful way to quantify the reaction kinetics.

Further reaction and interaction mechanisms are also important in these systems. The sorption of strontium in clay minerals and zeolites in particular is not well understood, although various spectroscopic techniques (EXAFS, XAS) have been implemented in an attempt to discern both the coordination of strontium species as well as the degree of hydration. While solid-state NMR is one of the most effective techniques for developing a molecular-level understanding of cation sorption, the low gyromagnetic ratio and low natural abundance of the NMR-active strontium isotope make it difficult experimentally to acquire and interpret solid-state ^{87}Sr NMR spectra. Therefore, additional studies have been designed to (a) identify the effects of strontium on the kinetics of neophase formation and (b) probe the coordination environment of strontium nuclei trapped in these phases using solid-state NMR. Simulated neophases have been generated by seeding a model Hanford waste solution with colloidal silica in the presence of varying concentrations of cesium, strontium, and iodine. Aluminum, silicon, and sodium MAS NMR are used to follow the kinetics of neophase formation and the impact of the strontium concentration on these kinetics. NMR methods for probing strontium nuclei will also be discussed, offering useful experimental approaches for the direct NMR analysis of strontium in neoformed precipitates and other systems of environmental importance.

NANOSTRUCTURATION OF PYRIDINE GUEST MOLECULES ENTRAPPED IN THE TUNNELS OF SEPIOLITE

Wenxing Kuang*, Glenn A. Facey, and Christian Detellier

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Sepiolite is a naturally occurring fibrous phyllosilicate structurally with nanotunnels (3.7 × 10.6 Å in cross section). Sepiolite is previously heated at 120 ºC to remove selectively the zeolitic and surface bound water molecules, and then exposed to pyridine vapor at room temperature. Two kinds of pyridine molecules are evidenced in the broad line ^{2}H NMR spectra: (i) mobile surface pyridine molecules easily removed by heating at 90 ^{o}C for a night, and (ii) rigid pyridine molecules trapped in the nanostructured tunnels of sepiolite and H-bonded with structural water. Upon further heating of the sample, the structural water is entirely removed along with some of the pyridine molecules. The ^{15}N chemical shielding parameters indicate that the remaining pyridine replaces the structural water and is coordinated directly to the edge Mg^{2+} sites.