ADSORBATES AT MINERAL SURFACES

Monday June 21, 2004

Adsorbates at Mineral Surfaces I	
2:00 – 2:20p	**EFFECT OF INTERLAYER CATION ON DEHYDROCHLORINATION OF POLYCHLORINATED ETHANES BY REDOX-MANIPULATED SMECTITE CLAY MINERALS**. Javiera Cervini-Silva[*1], Richard A. Larson[2], and Joseph W. Stucki[2] [1]Department of Earth and Planetary Sciences, University of California, Berkeley, CA 94720-3110, [2]Department of Natural Resources and Environmental Sciences, University of Illinois Urbana, IL 61801
2:20 – 2:40p	**PROBING OXYANION ADSORPTION MECHANISMS AT THE MINERAL/WATER INTERFACE WITH MOLECULAR-SCALE TECHNIQUES.** Derek Peak University of Saskatchewan, Department of Soil Science, 51 Campus Drive, Saskatoon SK, S7N 5A8 Canada
2:40 – 3:00p	**MOLECULAR-LEVEL INVESTIGATION OF METAL INTERACTIONS WITH CLAY MINERALS.** Daniel G. Strawn[*], Luca Furnare University of Idaho, Moscow, ID
Adsorbates at Mineral Surfaces II	
3:20 – 4:00p	**MASS AND CHARGE TRANSPORT IN LAYERED DOUBLE HYDROXIDE MODIFIED ELECTRODES.** Roto Roto and Gilles Villemure[*] Department of Chemistry, University of New Brunswick, P.O. Box 45222, Fredericton, New Brunswick, Canada E3B 6L2
4:00 – 4:20p	**STEREOSELECTIVE PHOTOOXIDATION OF SULFIDE BY USE OF CLAY-CHIRAL METAL COMPLEX ADDUCTS AS A PHOTOSENSITIVE ADSORBENT.** Shuji Fujita[1], Hisako Sato[1,2], and Akihiko Yamagishi[*1,2] [1]Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo; [2]CREST, Japan Science and Technology Corporation
4:20 – 4:40p	**SYNTHESIS AND CHARACTERIZATION OF CLAYS AND ORGANOCLAYS FOR THE SELECTIVE ADSORPTION OF N-NITROSAMINES.** Anibal Quintana[*] and Antonio S. Lara New Mexico State University, Department of Chemistry and Biochemistry, P.O. Box 3C, Dept. 3001, Las Cruces, NM 88003
4:40 – 5:00p	**FACTORS AFFECTING THE DESORPTION OF CADMIUM FROM GOETHITE.** Ghulam Mustafa[1], Balwant Singh[*1], and Rai Singh Kookana[2] [1]Faculty of Agriculture, Food and Natural Resources, The University of Sydney, Sydney, NSW 2006, Australia; [2]CSIRO Land and Water, PMB 2, Glen Osmond, SA 5064, Australia

Adsorbates at Mineral Surfaces Poster Session	
5:00p	**INVESTIGATING THE MOLECULAR INTERACTIONS OF OXYTETRACYCLINE IN CLAY AND ORGANIC MATTER: INSIGHTS ON FACTORS AFFECTING ITS MOBILITY IN SOIL.** Pankaj Kulshrestha*, Rossman F. Giese, and Diana S. Aga. Department of Geology, The State University of New York, Buffalo, NY 14260
	QCM STUDIES ON ADSORPTION BY AN ION-EXCHANGE ADDUCT. Masataka Komatsu[1], Saruwatari Kazuko[1], and Akihiko Yamagishi[1,2]* [1]Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo; [2]CREST, Japan Science and Technology Corporation

MONDAY JUNE 21, 2004

ADSORBATES AT MINERAL SURFACES I

1:20PM

EFFECT OF INTERLAYER CATION ON DEHYDROCHLORINATION OF POLYCHLORINATED ETHANES BY REDOX-MANIPULATED SMECTITE CLAY MINERALS

Javiera Cervini-Silva[*1], Richard A. Larson[2], and Joseph W. Stucki[2]

[1]Department of Earth and Planetary Sciences, University of California, Berkeley, CA 94720-3110, [2]Department of Natural Resources and Environmental Sciences, University of Illinois Urbana, IL 61801

Potassium fixation is an important process in clay soils and sediments. This paper reports the effect of Na^+-for-K^+ exchange in redox-manipulated Upton montmorillonite (Upton) or ferruginous smectite (SWa-1) on elimination reactions of pentachloroethane and 1,1,1-trichloroethane. Iron redox cycling in smectites were studied using reduced or reduced-reoxidized Upton or SWa-1 saturated with Na^+ or K^+ (Na^+-$Upton_R$ or Na^+-$Upton_{RO}$, K^+-$Upton_R$ or K^+-$Upton_{RO}$, Na^+-SWa_R or Na^+-SWa_{RO}, K^+-SWa_R or K^+-SWa_{RO}). Upon K^+-for-Na^+ exchange, Upton and SWa-1 showed incomplete reoxidation of structural Fe(II), possibly because of the collapse of superimposed clay layers precluding access to interlayer surfaces by the oxidizing agent. The transformation pathways of 1,1,1-trichloroethane and pentachloroethane depended on the oxidation state of the structural iron, and the nature of the clay and exchangeable cation. Regardless of the nature of the exchangeable cation, transformation of pentachloroethane was greater with SWa_R than with $Upton_R$, and with SWa_{RO} than with $Upton_{RO}$. Dehydrochlorination of pentachloroethane proceeded to a larger extent by K^+-$Upton_{RO}$ than by K^+-SWa_{RO}, but an opposite trend in reactivity prevailed when Na^+ was the exchangeable cation. The higher Fe(II) content in K^+-SWa-1 compared to K^+-Upton possibly contributes to impede reversible expansion of interlayer spacing upon reoxidation. Partially -collapsed, redox-manipulated smectites may owe their Brønsted-base behavior towards polychlorinated ethanes to more strongly adsorbed water at basal surfaces in the vicinity of octahedral Fe(II). Dehydrochlorination of 1,1,1-trichloroethane to 1,1-dichloroethene by SWa-1 occurred only with the K^+-SWa_R form, and, on a molar basis, led to a faster loss than observed for pentachloroethane with the same form of SWa-1. So, K^+ exchange led to increases in rates of transformation of pentachloroethane in mixed-valent SWa-1 and of 1,1,1-trichloroethane in SWa_R. In the case of pentachloroethane, these findings are opposite to the effect of K^+ on the reactivity of Fe(II) in SWa_R and $Upton_R$. Owing to the greater hydration energy of Na^+, K^+ may yield a lower water content adjacent to basal surfaces, and guarantee less energetic constraints for electron transfer between clay basal planes and 1,1,1-trichloroethane. Clearly, $E1_{cb}$ and E2 reactions of polychlorinated ethanes in redox-manipulated smectites occur at different clay sites. These findings add complexity to the effects of interlayer cations and surface-water on charge transfer from the clay to organic solutes in suspension.

PROBING OXYANION ADSORPTION MECHANISMS AT THE MINERAL/WATER INTERFACE WITH MOLECULAR-SCALE TECHNIQUES

Derek Peak

University of Saskatchewan, Department of Soil Science, 51 Campus Drive, Saskatoon SK, S7N 5A8 Canada

Many different oxyanions are found in the soil environment, and the chemistry of these oxyanions is quite varied. Oxyanions are studied for both agronomic and environmental reasons by soil chemists. Some oxyanions such as phosphate and sulfate are essential nutrients for plant growth and are found in relatively high concentrations in soils. Other oxyanions such as borate and molybdate are micronutrients. They are essential for plant growth at low concentrations but become toxic at higher concentrations. The range between deficiency symptoms and toxicity is usually quite narrow. A third group of oxyanions, such as arsenate, arsenite, selenate, selenite, and chromate are frequently studied because they have little agronomic use and are instead detrimental to human health. Understanding the mechanisms by which these oxyanions react with mineral surfaces is vital for predicting their bioavailability, toxicity, and transport in natural systems.

The environmental soil chemistry program at University of Saskatchewan uses an array of advanced spectroscopic techniques to determine the nature of interactions between oxyanions and soil components. Several types of X-Ray Absorption Spectroscopy (XAS) have been utilized as well as Attenuated Total Reflectance (ATR) FTIR spectroscopy. While the mechanisms of adsorption are unique to both the sorbate and sorbent being studied, there is a recurring theme in that is quite significant.

In many cases, more than one adsorption mechanism can be seen to occur simultaneously. In systems where only adsorption is occurring, then both outer-sphere and inner-sphere complexation are often observed at the same time. This distribution of outer-sphere and inner-sphere surface complexes has been seen with sulfate, selenate, and borate on iron oxides. Reaction conditions such as pH, ionic strength, surface structure of sorbent, and reactant concentration have all been shown to influence the relative distribution of the simultaneously occurring sorption complexes. Therefore it is necessary to conduct spectroscopic studies at a wide range of reaction conditions to truly understand the reactivity of oxyanions. It is also important to account for outer-sphere complexation of oxyanions when attempting to describe their adsorption with surface complexation models.

MOLECULAR-LEVEL INVESTIGATION OF METAL INTERACTIONS WITH CLAY MINERALS

Daniel G. Strawn*, Luca Furnare

University of Idaho, Moscow, ID

Clay minerals have tremendous sorption capacities for cations, and thus play a major role in the biogeochemical reactions occurring in natural systems. Metal cations, such as copper and lead, are selectively adsorbed by clay minerals in the environment. The goal of this project is to characterize copper reaction mechanisms with clay minerals under varying equilibrium conditions. To accomplish this we probed the molecular environment of sorbed Cu using X-ray absorption fine structure (XAFS) spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, and X-ray diffraction (XRD). The variables studied include ionic strength and background electrolyte, pH, clay mineral type, and reduction state. The clay minerals studied were a Wyoming montmorillonite, Llano vermiculite, and reduced South African (Palabora) vermiculite. At low ionic strength and in the presence of no background electrolytes, Cu sorption mechanisms on all clay minerals were dominated by outer-sphere complexation, confirming that classic cation exchange processes are occurring. However, in the presence of Ca or K background electrolytes at high ionic strengths (0.1 M) inner-sphere complexation was the predominant reaction complex. The type of inner-sphere complexation mechanism varied depending on the clay mineral species. On montmorillonite small surface precipitates were observed, on Llano vermiculite monodentate adsorption on the edge sites were occurring, and on the reduced SA vermiculite Cu was adsorbing over the ditrigonal cavities present on the basal planes to satisfy the reduced positive charge associated with structural iron reduction. Our results did not reveal the formation of extensive layered double hydroxides or metal-clay neosynthesis products that have been reported in the literature for Ni, Zn, or Co. Our results provide new information on the reaction processes by which metals can interact with clay minerals, and will aid in designing remediation strategies, predicting bioavailability, and monitoring and managing contaminated sites.

MONDAY JUNE 21, 2004

ADSORBATES AT MINERAL SURFACES II

3:20PM

MASS AND CHARGE TRANSPORT IN LAYERED DOUBLE HYDROXIDE MODIFIED ELECTRODES

Roto Roto and Gilles Villemure*

Department of Chemistry, University of New Brunswick, P.O. Box 45222, Fredericton, New Brunswick, Canada E3B 6L2

Recent results of our study of charge transport in thin films of a redox active Ni-Al-Cl LDH will be presented. Impedance measurements show that the charge-transfer resistance of Ni-Al-Cl films decreased dramatically upon oxidation of nickel, from more than 10^6 Ω for un-oxidized films to less than 60 Ω in films oxidized to $Ni^{2.5+}$. At low frequency, the impedance of the oxidized films was dominated by mass transport. Effective diffusion coefficients estimated from the low frequency impedance varied between 1 and 5 x 10^{-9} cm^2/s. For Mg-Mn-CO_3 films, partial oxidation of the Mn(III) sites resulted in a similar drop in charge-transfer resistance. However, the charge-transfer resistance increased up to nearly its initial value in Mg-Mn-CO_3 films in which the manganese had been fully oxidized to Mn(IV).

Mass measurement using an electrochemical quartz crystal microbalance showed that the Ni-Al-Cl films lost mass on oxidation and gained mass on reduction. Impedance measurements at the resonance frequency of the LDH coated quartz crystals show that Sauerbrey's equation was valid for this system. The sizes of the mass change depended on the pH and composition of the electrolyte solutions. In a pH 8 potassium borate buffer, an apparent mass per mole of electrons transferred (MPE) of only 6 g/mol was obtained. Compensation for the positive charges generated by oxidation of the LDH's Ni(II) sites appear to occur by loss of protons from the LDH lattice accompanied by the loss of some water from the interlayer spaces. In pH 8 potassium borate buffer containing 4 mM Na^+ the MPE increased to 19 g/mol, suggesting that, in the presence of sodium, charge neutralization shifted from gain/loss of protons to intercalation/de-intercalation of sodium ions. Addition of $[Fe(CN)_6]^{4-}$ or $[Mo(CN)_8]^{4-}$ to the electrolyte solutions caused mass increases due to the intercalation of the heavy anions in the LDH films. Oxidation of the adsorbed anions resulted in reversible mass drops. Charge neutrality was maintained by desorption and re-adsorption of the electrolyte cations.

The cyclic voltammograms of $[M(bpy)_3]^{2+}$ (M = Os, Ru and Co) solutions at Ni-Al-Cl LDH modified electrodes were recorded. For $[Os(bpy)_3]^{2+}$, the cathodic peak current obtained with the Ni-Al-Cl coated electrode was 50 times larger than with the unmodified substrate. Addition of a small amount of $[Ru(bpy)_3]^{2+}$ resulted in an additional 2-fold increase in the size of the $[Os(bpy)_3]^{2+}$ reduction peak. Addition of $[Ru(bpy)_3]^{2+}$ to a solution of $[Co(bpy)_3]^{2+}$ produced a similar increase in the $[Co(bpy)_3]^{2+}$ reduction peak. In mixtures of all three cations however, the enhancement of the $[Co(bpy)_3]^{2+}$ voltammetric wave was suppressed at the expense of the $[Os(bpy)_3]^{2+}$ wave. These results were unexpected. These cationic species had not been expected to interact with the positively charged layers in LDH films.

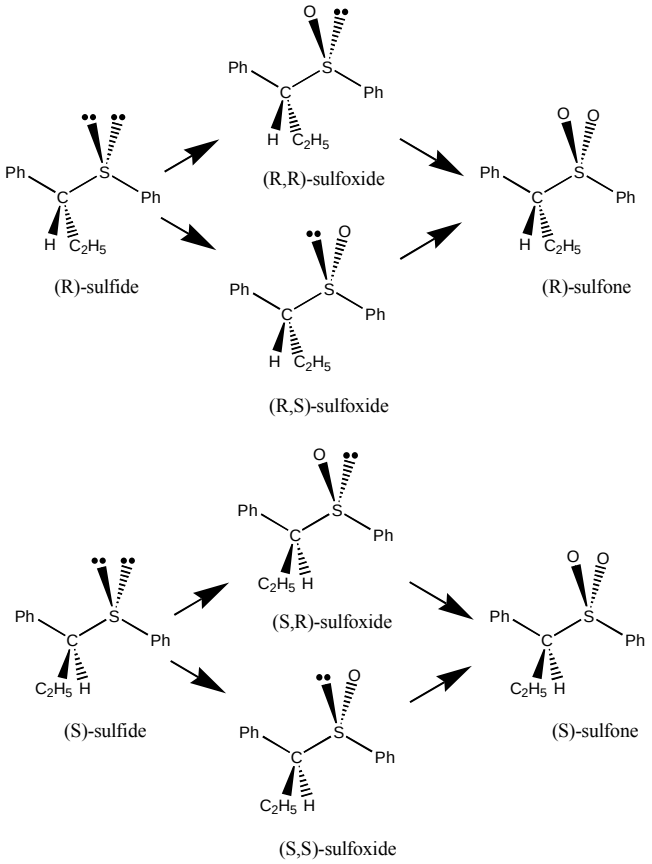
STEREOSELECTIVE PHOTOOXIDATION OF SULFIDE BY USE OF CLAY-CHIRAL METAL COMPLEX ADDUCTS AS A PHOTOSENSITIVE ADSORBENT

Shuji Fujita[1], Hisako Sato[1,2], and Akihiko Yamagishi[*1,2]

[1]Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo ; [2]CREST, Japan Science and Technology Corporation

We have attempted the photooxidation of a prochiral sulfide by using a clay mineral modified by photosensitive chiral metal complexes, $[Ru(bpy)_3]^{2+}$and $[Ru(phen)_3]^{2+}$. A sulfide used in this research has a chiral carbon. By identifying four kinds of prodcuts, both enantiomeric and diastereomeric selectivity were observed. We discussed the interactions among the chiral carbon center of a substrate, adsorbed metal complexes and a clay surface.

We used α-ethylbenzyl phenyl sulfide as a substrate. It has an asymmetric carbon. The sulfide is oxidized in two stages; a sulfide to a sulfoxide at the first stage and a sulfoxide to a sulfone at the second stage. Since a sulfur in a sulfoxide is chiral, two enantiomeric pairs are produced from the present substrate (Scheme 1) in which each pair is in diastereomeric relation (Figure1).



Scheme 1. Oxidation of α-ethylbenzyl phenyl sulfide

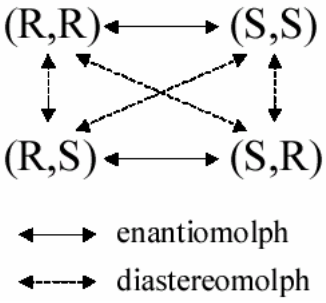


Figure 1. Stereomolph of the sulfoxide

SYNTHESIS AND CHARACTERIZATION OF CLAYS AND ORGANOCLAYS FOR THE SELECTIVE ADSORPTION OF N-NITROSAMINES

Anibal Quintana* and Antonio S. Lara

New Mexico State University, Department of Chemistry and Biochemistry, P.O. Box 3C, Dept. 3001, Las Cruces, NM 88003

N-Nitrosamines are among the most toxic compounds in tobacco smoke. Seven of the top ten tumorigenic compounds in tobacco smoke are N-nitrosamines. These compounds can reach the respiratory tract, lungs and alveolar tissue within the lungs. The high incidence of cancer among tobacco smokers is proof enough that these compounds are not trapped by the common cigarette filter. The goal of this research is to study the adsorption of N-nitrosamines onto sodium exchanged clays and organoclays.

Clays and organoclays were used as adsorbent materials in order to trap/sorb the carcinogenic N-nitrosamines. The large surface area, known potential to adsorb organics and ease of modification of clays makes them suitable materials. A major contributing factor for the selective adsorption of N-nitrosamines is the natural charge of clay particles. For these reasons, two smectite clays (STx-1 and SAz-1) of differing cation exchange capacities were selected as N-nitrosamine adsorbent materials. For purpose of specific adsorption, clays were modified with a homologous series of tetra-alkylammonium cations in order to study the alternate adsorption interactions between these modified clays and the N-nitrosamines. The changes in surface area, basal spacing, thermal and carbon/nitrogen elemental analysis indicated the presence of new porous and non-porous organoclay materials. Models were proposed to describe the adsorption of N-nitrosamines. The proposed models include ion-permanent dipole and additive London dispersive attractive forces, these to include surface, multi-sided, and pore interactions.

Besides the characterizations noted above, adsorption processes were characterize by Infinite Dilution Inverse Gas Chromatography. This will facilitate the understanding/proposing mechanisms for the adsorption of N-nitrosamines on the clay adsorbent materials. This technique was used to calculate the enthalpy, entropy and Gibbs free energy for the N-nitrosamine/clay adsorbent interaction. The enthalpy range for the adsorption of N-nitrosamines onto sodium homoionic clays and organoclays is -41 to -87 kJ/mol and -60 to -90 kJ/mol, respectively.

Theoretical calculations for the structural and molecular dimensions of the clay adsorbent materials and N-nitrosamines, respectively, were used to complement the proposed adsorption models. The structural dimensions and physicochemical properties of the clay materials were correlated to develop topographical models. These models were subsequently further correlated to molecular dimensions of the N-nitrosamines in order to complement the proposed adsorption mechanisms – natural sodium clays, porous and non-porous organoclays. Experimental and theoretical results indicate that clays and organoclays are effective in adsorbing and even selectively trapping N-nitrosamines.

FACTORS AFFECTING THE DESORPTION OF CADMIUM FROM GOETHITE

Ghulam Mustafa[1], Balwant Singh[*1], and Rai Singh Kookana[2]

[1]Faculty of Agriculture, Food and Natural Resources, The University of Sydney, Sydney, NSW 2006, Australia; [2]CSIRO Land and Water, PMB 2, Glen Osmond, SA 5064, Australia

Cadmium is perhaps environmentally the most significant heavy metal in soils. Bioavailability and fate of Cd entering in soils is usually controlled by adsorption-desorption reactions on Fe oxides. Adsorption of Cd on soil colloids including Fe oxides has been extensively studied but Cd desorption from soil minerals has received relatively little attention. Some factors that affect Cd adsorption on goethite include pH, temperature, aging and presence of inorganic and organic ions. This research was conducted to study the influence of pH**,** temperature, aging, desferrioxamine B and oxalic acid on Cd desorption from goethite.

Two batch experiments were conducted to evaluate Cd desorption with 0.01 M $Ca(NO_3)_2$ from goethite. In the first experiment, Cd desorption was observed at 20, 40 and 70 °C in combination with aging for a period of 16 hours, 30, 90 and 180 days using goethite with Cd adsorbed from initial Cd concentrations of 20, 80 and 180 µM. Cadmium desorption for all these treatments was measured at pH 5.5 and 6.0. In the second experiment, Cd desorption was determined separately in the presence of 300 µM desferrioxamine B (DFOB), 200 µM oxalic acid (OA) and the combination of two at 25 °C. For the second desorption experiment goethite samples which adsorbed Cd from initial Cd concentrations of 180 and 300 µM at pH 6.0 were used.

At the lowest amount of initially adsorbed Cd and equilibrium pH 5.5, Cd desorption decreased from 71 to 17% with aging from 16 hours to 180 days and the corresponding decrease at pH 6.0 was from 32 to 3%. There was a substantial decrease in Cd desorption with increase in equilibration temperature. For example, in goethite with the lowest amount of initially adsorbed Cd after 16 hr and at equilibrium pH 5.5, Cd desorption decreased from 71 to 31 % with increase in temperature from 20 to 70°C. Dissolution of Cd adsorbed goethites in 1 M HCl, after 15 successive desorptions with 0.01 M $Ca(NO_3)_2$, indicated that approximately 60% of the Cd is surface sorbed.

Cadmium desorption increased in the presence of DFOB, OA and DFOB + OA. The dissolution of goethite in presence of DFOB possibly increased Cd desorption whereas a decrease in equilibrium pH from 6.0 to 4.8 was the main factor for increased Cd desorption in the presence of OA.

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POSTER SESSION

5:00PM

INVESTIGATING THE MOLECULAR INTERACTIONS OF OXYTETRACYCLINE IN CLAY AND ORGANIC MATTER: INSIGHTS ON FACTORS AFFECTING ITS MOBILITY IN SOIL

Pankaj Kulshrestha*, Rossman F. Giese, and Diana S. Aga.

Department of Geology, The State University of New York, Buffalo, NY 14260

Residual concentrations of tetracycline antibiotics in the environment have been found to contaminate surface, ground and drinking water, aquatic sediments and soils. This has also led to increased emergence of resistant strains of pathogenic bacteria that could potentially impact human health. The interactions of oxytetracycline with model clay adsorbents and organic matter were investigated as a function of suspension pH. The clay adsorbents used were the montmorillonite clay (SWy-2), Na-montmorillonite clay (Na-SWy-2), and hexadecyl trimethyl ammonium-montmorillonite clay (HDTMA-clay). The adsorption of oxytetracycline to the clay could be described by Freundlich type adsorption isotherms. It was observed that the adsorption of oxytetracycline in the natural and sodium forms of montmorillonite clay decreases with increasing pH in the order pH 1.5 > pH 5.0 > pH 8.7 > pH 11.0. This trend is consistent with cationic exchange interactions that are dominant at lower pH values when oxytetracycline has a net positive charge. On the other hand, hydrophobic interactions when oxytetracycline is zwitterionic (at pH 5.0) are predominant, as evident from the FT-IR spectrum of the HDTMA-clay adsorbed with oxytetracycline. The presence of large amount of dissolved organic matter (DOM) was also found to decrease the sorption of oxytetracycline on clay, suggesting that DOM may increase its mobility in the natural environment. Several mechanisms of interaction of oxytetracycline in clay are proposed based on the adsorption isotherms and the results from X-ray diffraction (XRD) and Fourier transformed infrared (FT-IR) analyses.

QCM STUDIES ON ADSORPTION BY AN ION-EXCHANGE ADDUCT

Masataka Komatsu[1], Saruwatari Kazuko[1], and Akihiko Yamagishi[1,2]*

[1]Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo; [2]CREST, Japan Science and Technology Corporation

An ion-exchange adduct of Mg-Al layered double hydroxide and $[Fe(BPS)_3]^4$-(BPS = 4,7-diphenyl-1,10-phenanthroline disulfonate) was prepared by the coprecipitation method at various Mg(II)-to-Al(II) ratios ([Mg(II)]/[Al(III)] = 2/1, 3/1 and 4/1). The structures and adsorption properties of the materials were studied by XRD, TG and QCM (quartz crystal microbalance) measurements. LDH-$[Fe(BPS)_3]$ was prepared by the coprecipitation method which was thought to be effective for a bulky anion. An aqueous suspension of an ion-exchange adduct was cast onto a gold-coated quartz electrode (an 1.33 cm^2 electrode area) and dried under air. The electrode was immersed in an aqueous solution. The change of mass was monitored by following resonance frequency (Δf) after adding organic liquid as an adsorbate under stirring. Mass change was calculated according the following Sauerbrey equation: $\Delta m = S\Delta f$ ($S = -17.7$ ng $Hz^{-1}cm^{-2}$). Figure 1 shows an example of the QCM measurements when acetonitrile was added to the water medium in which a QCM electrode was immersed. The saturated adsorption amount was calculated to be 9.21×10^3ng per 1 mg of the adduct. Similar experiments were performed for other kinds of organic molecules to examine any selectivity towards an adsorbate.

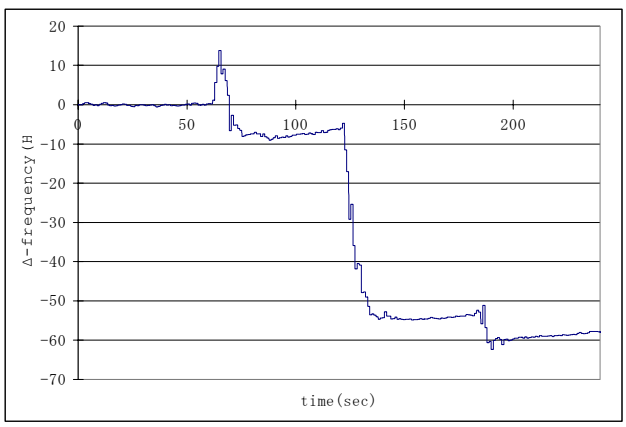

Figure.1 The frequency change of a QCM electrode coated with a cast film of an adduct of LDH (Mg/Al = 4/1) with $[Fe(BPS)_3]^{4-}$.