

Chemistry Seminar Abstracts for Fall 2017

Geochemistry and the Exploration for New Metal Deposits	2
Marek Locmelis, Dept. of Geosciences & Geological & Petroleum Engineering, MS&T	
Atomic Motion Under the Microscope- Controlling and Analyzing Few-body Dynamics.....	2
Daniel Fischer, Dept. of Physics, MS&T	
Role of Mössbauer Spectroscopy and X-ray Diffraction in the Study of Prussian Blue Pigment Fading.....	3
Gary J. Long, Dept. of Chem., MS&T	
Cancer Biomarker Discovery Using Urinary Metabolomics and Advanced Analytical Techniques: Achievement and New Challenges.....	4
Yinfa, Center for Biomedical Reserach, Dept. of Chem., MS&T	
Drug the Undruggable: from Nature to Precision Cancer Medicine.....	4
Liang Xu, Dept. of Molecular Biosciences & Dept. of Radiation Oncology, University of Kansas	
Microwave Spectroscopic Models for Hydrogen Storage in Metal Organic Frameworks	5
Stewart E. Novick with Daniel A. Obenchain, G.S. Grubbs II, and Herbert M. Pickett, Departments of Chemistry Wesleyan University Middletown, Connecticut, and MS&T	
Epitaxial Lift-off of Electrodeposited Single-Crystal Gold Foils for Flexible Electronics.....	5
Jay A. Switzer, Dept. of Chem. & Graduate Center for Materials Research, MS&T	
pH Measurements Using Fluorine-19 NMR Spectroscopy	6
Ming Huan, Dept. of Chem., MS&T	
Harmful Algal Blooms: Symptoms of Ecological Imbalance & Ecosystem Integration	6
Dr. Keith Loftin, Organic Geochmistry Research Laboratory & U.S. Geological Survey, Lawrence, KS	

Geochemistry and the Exploration for New Metal Deposits

Marek Locmelis, Dept. of Geosciences & Geological & Petroleum Engineering, MS&T

Abstract: Magmatic sulfide ore deposits are an important source of metals such as nickel, copper and platinum-group elements. However, a decline in new world-class ore deposit discoveries in recent years suggests that most of the easily recognizable deposits have already been found. As a consequence, there is a high demand for innovative approaches that may guide future exploration efforts.

This presentation will provide an introduction to the development of geochemical exploration tools and discuss the active research in this field in the Department of Geosciences and Geological and Petroleum Engineering at Missouri S&T. A particular focus will be on the use of mineral trace element chemistry in the exploration for magmatic nickel sulfide deposits.

Exploration techniques based on mineral chemistry have an advantage over traditional bulk-rock methods as ore-forming signatures recorded in alteration-/weathering resistant minerals are harder to erase than in bulk-rocks. In the past, exploration approaches using trace element variation patterns in minerals have often been neglected in the search for magmatic metal sulfide deposits due to analytical limitations. However, modern laser ablation ICP-MS techniques have lowered the detection limits for many trace elements as much as an order of magnitude. This presentation will discuss how an entirely new generation of mineral-based geochemical exploration tools is currently being developed using laser ablation ICP-MS.

Atomic Motion Under the Microscope- Controlling and Analyzing Few-body Dynamics

Daniel Fischer, Dept. of Physics, MS&T

Abstract: Understanding the dynamics in systems of several interacting particles is one of the key challenges of physics. Such systems generally cannot be described in closed analytical form as soon as more than two particles are involved. This dilemma is well-known as the "few-body problem" which sets us close limits to accurately predicting a many-particle system's state. Therefore, the advancement of our knowledge of phenomena that emerge due to the complex interplay of several particles requires the joined theoretical and experimental exploration for a wide range of situations. The fragmentation of atoms due to the interaction with charged projectiles, with photon, or with strong external fields represent an ideal test ground of few-body physics for several reasons: First, few-body effects in these systems are ubiquitous and relevant to many research fields and numerous technical applications, particularly in areas such as materials science, quantum chemistry, biological science, and information processing. Second, advanced experimental techniques are available which allow manipulation of the parameters of the few-particle quantum state with a high degree of control and accuracy. Moreover, modern

spectrometers enable snapshots to be taken of the state's change over time, allowing details of the state's dynamics to be analyzed.

At MS&T, there is an experiment in preparation that combines the most advanced experimental methods for the control and analysis of atomic few-body systems in a single apparatus: Using laser cooling and manipulation techniques, a large variety of initial states are created, ranging from single excited or polarized lithium atoms to large ensembles of atoms that are cooled down to micro-Kelvin temperatures and even to quantum-degeneracy. For the analysis, a "reaction microscope" will be employed allowing the coincident measurements of the momentum vectors of atomic fragments after ionization of the atoms. In essence, there are three fundamental questions to be addressed in the experiments: First, how do the ionization dynamics depend on the relative orientation (or helicity) of an ionizing laser field and a polarized target atom? Such experiments will help to understand fundamental symmetries and ultimately control the interaction of laser fields with chiral (atomic or molecular) targets, which play a crucial role e.g. in biochemistry. Second, how is the disintegration of an atom due to the interaction with an ionizing field influenced by its environment? This is experimentally only studied for clusters or solid targets, but largely unexplored for more dilute systems. Apart from the fundamental importance of this question, the dependence of the ionization dynamics on the environment is relevant to the understanding of the damage of biological tissue due to radiation. Finally, how does the correlated wave function of a few-particle system change as a function of the particle number and interaction type and strength? The possibility to "engineer" simple few-body systems and observe such systems comprehensively would allow one to "simulate" and understand fundamental quantum phenomena that occur in natural or artificial material.

Role of Mössbauer Spectroscopy and X-ray Diffraction in the Study of Prussian Blue Pigment Fading

Gary J. Long, Dept. of Chem., MS&T

Abstract: The two Prussian blue compounds, the so-called "soluble" $\text{KFeIII}[\text{FeII}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ and "insoluble" $\text{FeIII}_4[\text{FeII}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ have long been important in understanding the intervalent charge transfer transitions observed in mixed valence compounds. This transition is responsible for the intense blue colour of the Prussian blue pigments often used by artists from shortly after their discovery in 1704 to well into the early twentieth century. Unfortunately, these pigments often fade with time when exposed to light. Our long-term goal has been to obtain a better understanding of this fading of "ancient" Prussian blue pigments. Although there is an extensive literature dealing with Prussian blues, it was soon apparent that there was vast variations in the Mössbauer-spectral properties reported for often unspecified or poorly characterized compounds or pigments. Thus in reaching our goal it soon became apparent that

we needed a far better understanding of the properties of modern Prussian blues and their associated pigments.

My talk will illustrate how we have obtained an improved understanding of the modern Prussian blue properties through a variety of experimental studies [1-6] and will concentrate on our Rietveld, pair-distribution, and Williamson-Hall strain analyses of high-resolution powder x-ray diffraction patterns of well characterized Prussian blues in order to explain why such a wide variation in their Mössbauer spectra is found in the literature. More specifically, our work has shown that the strain induced in Prussian blues through their extremely rapid precipitation from solution can account, at least in part, for the wide variation in their observed Mössbauer spectra.

Cancer Biomarker Discovery Using Urinary Metabolomics and Advanced Analytical Techniques: Achievement and New Challenges

Yinfa, Center for Biomedical Reserach, Dept. of Chem., MS&T

Abstract: Metabolomics has emerged as a transformative approach to cancer bio-marker discovery owing to the intimate connection between oncogenic transformation and cellular metabolism. Heightened focus on developing molecular biomarkers that may be screened using minimally invasive point-of-care assays has prompted serious efforts into the application of urinary metabolomics for early cancer detection. Current research efforts have identified a multitude of putative metabolic biomarkers with limited clinical performance which has been attributed to challenges in urine normalization, natural metabolic variations, and poor disease specificity. Our research team has proposed the novel application of multi-marker panels that combine molecular biomarkers with clinically relevant patient information to improve biomarker performance. The biomarker panels, techniques, clinical results, and challenges, will be presented at the seminar..

Drug the Undruggable: from Nature to Precision Cancer Medicine

Liang Xu, Dept. of Molecular Biosciences & Dept. of Radiation Oncology, University of Kansas

Abstract: The RNA-binding proteins (RBPs) Musashi-1 (Msi1) and Hu antigen R (HuR) are emerging therapeutic targets for cancer and cancer stem cells. So far there is limited success on small molecules that directly inhibit Msi1 and HuR. RBPs such as Msi1 and HuR are considered "undruggable" due to the lack of a well-defined binding pocket for target RNA. Since relocation to the University of Kansas in 2010, I established a multidisciplinary cancer drug discovery team

to "drug the undruggable" Msi1 and HuR. Through a contemporary, structure-based, multidisciplinary and integrated drug discovery approach, we identified promising hits and initial lead compounds with sub-microM K_i values. With two funded NCI R01 grants and one DOD grant, we are employing structure-based rational design for lead optimization and target validation to discover novel compounds that inhibit the so far undruggable Msi1 and HuR, aiming to develop it as an entirely new class of molecular-targeted anti-cancer drugs.

Microwave Spectroscopic Models for Hydrogen Storage in Metal Organic Frameworks

Stewart E. Novick with Daniel A. Obenchain, G.S. Grubbs II, and Herbert M. Pickett, Departments of Chemistry Wesleyan University Middletown, Connecticut, and MS&T

Abstract: The microwave spectra of molecular hydrogen bound to metal halides, including H_2 CuF, H_2 AgCl, HD AgCl, D_2 AgCl, H_2 AuCl, and H_2 CuCl, have been studied using Cavity Fourier transform microwave (FTMW) spectroscopy. The complexes are T-shaped with the H-H as the cross of the T with the metal atom closest to the hydrogen. The molecular hydrogen is bound to the metal strongly enough such that the properties (bond lengths and electronic environments) of the binding partners are perturbed from their monomeric values, but not so strongly that the H-H bond breaks to form dihydrides with the metal. We suggest that H_2 binds in this way to metal centers in metal organic frameworks (MOFs), which can be utilized to store hydrogen gas.

Epitaxial Lift-off of Electrodeposited Single-Crystal Gold Foils for Flexible Electronics

Jay A. Switzer, Dept. of Chem. & Graduate Center for Materials Research, MS&T

Abstract: Single-crystal silicon is the industry standard for electronic devices because of its high crystalline order and abundance. However, the brittle nature of bulk silicon precludes its use in flexible electronics. I will discuss a simple and inexpensive procedure for epitaxial lift-off of wafer-size flexible and transparent foils of single-crystal Au using Si(111) as a template. Lateral electrochemical undergrowth of a sacrificial SiO_x layer was achieved by photoelectrochemically oxidizing n-Si(111) under light irradiation. Cu_2O as an inorganic semiconductor was epitaxially electrodeposited onto the Au foils, which showed a more ideal diode quality factor of 1.6 (where $n=1$ is ideal) than the value of 3.1 observed for a polycrystalline deposit. ZnO nanowires electrodeposited epitaxially on a Au foil showed flexibility with the nanowires intact up to 500 bending cycles. A 28 nm Au foil with a sheet resistance of $7 \Omega \cdot sq^{-1}$ showed only a 4% increase in resistance after 4000 bending cycles. A flexible organic light-emitting diode based on tris(bipyridyl)ruthenium(II) was spin-coated on a foil to exploit the transmittance and flexibility of the gold foil. The simple epitaxial lift-off procedure produces single-crystal Au foils that offer

the order of traditional semiconductors such as Si wafers without the constraint of a rigid substrate.

pH Measurements Using Fluorine-19 NMR Spectroscopy

Ming Huan, Dept. of Chem., MS&T

Abstract: The pH of an NMR sample can be measured directly by NMR experiments of signal intensities, chemical shift, or relaxation time constants that depend on the pH. In the work presented here, an NMR technique was utilized based on ^{19}F chemical shifts. For example, the chemical shift of the anion F in aqueous NaF or KF solutions changes throughout the range of pH 1 to 14 but most pronounced in the acidic range between pH =1 and 5. Adding F^- as a micro-sensor compound to solutions in NMR tubes makes it possible to accurately determine pH value in situ from ^{19}F chemical shifts. Because pH micro-sensor compounds added to an aqueous solution have an influence on the pH, only a minimum amount of an NMR micro-sensor compound should be added to the sample. A minimum number of 4×10^{16} nuclei was found to be sufficient for NMR signal observation using a 400-MHz spectrometer. Temperature-dependent NMR experiments were conducted to establish calibration curves through which the influence of temperature on the chemical shift can be corrected. The ^{19}F signal of external reference solution (trifluoroacetic acid) was found to have the least temperature-dependent chemical-shift variation and is suggested as independent standard for temperature-correction curves.

Harmful Algal Blooms: Symptoms of Ecological Imbalance & Ecosystem Integration

Dr. Keith Loftin, Organic Geochemistry Research Laboratory & U.S. Geological Survey, Lawrence, KS

Abstract: Cyanobacterial harmful algal blooms (CyanoHABs), currently (2017) appear to be the dominant type of HABs in inland waters of the U.S. In addition to causing ecological impairment and aesthetic issues, cyanoHABs can also produce a range of toxins with a range of symptoms including dermatitis, gastroenteritis, respiratory system depression, and even death in extreme cases of exposed animals and humans. Research published over the last decade has demonstrated that cyanotoxins and cyanoHABs are found across the country in every surface water type including lakes, reservoirs, rivers and streams, wetlands, and coastal waters at concentrations of human and ecological health concern. An U.S. Federal and State agency collaboration called CyAN (Cyanobacteria Assessment Network) is developing a national HAB database and satellite network attempting to provide early warnings of HAB events in lakes and reservoirs across the U.S. One objective of the CyAN project is to provide a systematic,

nationwide capability to evaluate HAB frequency, distribution, and magnitude over appropriate time scales for adaptive management. Most environmental issues are managed from a dissolved-phase contaminant standpoint which is publically invisible and resource intensive. HAB proliferation is a result of many adverse environmental issues we currently attempt to manage separately. Visible adverse outcomes such as HABs that are also scientifically measurable