MONTANA SECTION
OF THE AMERICAN CHEMICAL SOCIETY

PRESENTS THE

2013 SPRING MEETING

April 20, 2013

Montana Tech of The University of Montana
Butte, Montana

GENERAL SCHEDULE

8:00-9:00 am	**Social Time with Donuts, Coffee and Juice (1st Floor, Chemistry Biology Building)**
9:00-9:10 am	**Opening Remarks (Room 101)**
9:10-11:45 am	**Research Presentations** **SESSION A (Room 101)** **SESSION B (Room 102)** **SESSION C (Room 112)**
11:45-12:30 pm	**Lunch**
12:30-1:30 pm	**Keynote Address (Room 101)**
1:30-2:10 pm	**Research Presentations** **SESSION D (Room 101)** **SESSION E (Room 102)** **SESSION F (Room 112)**
2:10-2:40 pm	**Awards for best student presentation**
2:40 pm	**Board Meeting of the Montana Section of the American Chemical Society (2nd Floor Conference Rm)**

For further information about the Montana local section of the ACS please refer to our website:

http://montana.sites.acs.org

The American Chemical Society

The **American Chemical Society** (ACS), which is the professional organization for over 150,000 chemists, chemical engineers, and affiliated scientists:

- Promotes the public's perceptions and understanding of chemistry and the chemical sciences through public outreach programs and public awareness campaigns;
- Involves the Society's members in improving the public's perception of chemistry;
- Assists federal and state governments with advice on scientific and technological issues involving the chemical sciences;
- Enriches professionals in academia and private industry through development programs, peer interactions, and continuing educational courses;
- Hosts national, regional, and local section meetings for the exchanging of ideas; information and chemical research discoveries;
- Provides career development assistance and employment opportunities for students and professionals in academia and private industry;
- Fosters communication and understanding between members and the chemical industry, the government and the community to enhance the quality of scientific research, support economic progress, and insure public health and safety;

Session A (Room 101)

9:10 "Axial Chirality to increase selectivity of AIMs as anti-tumor agents." Michael J. Campbell (Undergraduate), Matthew J. Weaver and Nicholas R. Natale. The University of Montana**,** Missoula, MT 59812.

The focus of this project is to improve the efficacy of Anthracenyl isoxazolyl amides (AIMs) by adding axial chirality via strategic halogenation. AIMs are a new class of antitumor agents specially synthesized to bind and interact with G-quadruplex (G4) DNA; binding G4 DNA has been shown to repress the replication of oncogenes in cancerous tumors. By using asymmetric halogenation to introduce axial chirality into the AIMs, our goal is to create a molecule that is divided by a bond, or axis, that cannot freely rotate due to steric hindrance. Many biologically active molecules are chiral and the stereoisomers often display a significant difference in activity due to interactions with chiral targets, such as DNA. Our efforts are currently centered on over halogenating the anthracene followed by selective cleavage. Over halogenation of unsubstituted anthracenes in synthetically significant yields has been published by Cakmak. However, with the added complexity of the substituted anthracene used as a starting material in the production of the AIMs, the addition of halogens has become quite a challenge. We have successfully isolated a 1,2,3,4,10-pentabromo-anthracenyl-nitrile oxide. The original methods by which we synthesized this compound proved to be inefficient and require optimization. The future focus will then shift to optimization of the cycloaddition and methods of selective cleavage. The benefit of stereospecific activity is that a patient may be able to take less of the chemotherapeutic agent and achieve equally beneficial results with fewer side effects. Our progress will be described.

9:30 "Rivertop Renewables, Montana Based Company Commercializing a Nitric Acid Oxidation Process." Steve Rowley (Process Chemist), Don Kiely, Tyler Smith, Steve Donen. Rivertop Renewables, 1121 East Broadway, Missoula, MT 59802.

Rivertop Renewables is a Missoula-based progressive chemistry company that is commercializing a process that uses nitric acid to oxidize renewable feedstocks and produce novel building-block aldaric acids. Rivertop's patented technology has allowed it to become the first company to manufacture glucaric acid at commodity chemical cost mainly by eliminating cost prohibitive obstacles from a long known but poorly understood traditional process. These obstacles, and Rivertop's technology, will be discussed. The analytical methods that Rivertop has employed to understand this complicated reaction system will be shown and new insights to the reaction system's mechanism will be given.

9:50 "Synthesis and study of a novel family of conjugated carbazole centered compounds with potential applications in organic light-emitting diodes (OLEDs)." Myunghoon Kim (Undergraduate), Caroline Pharr. Carroll College, Helena, MT.

Organic Light-Emitting Diodes (OLEDs) have been of great interest in various technological applications. Currently, there have been many successful syntheses of stable organic compounds capable of emitting red and green light. However, synthesis of stable blue light-emitting compounds has proven to be challenging. Synthesis of a novel family of carbazole centered

molecules is underway with hopes of creating a stable blue light emitter. The parent compound is comprised of three subunit molecules, which to date have been synthesized : 4-bromodiphenylacetylene, 2,7-dibromocarbazole, and 1-(2`,3`,4`,5`-tetraphenyl)phenyl-4-bromobenzene (Dendron). Currently, a one-pot Suzuki-Miyaura cross-coupling containing magnesium diheteroarylboronate intermediates is being carried out to link the subunit molecules together and yield the parent compound of interest. Upon synthesis of the parent molecule, its properties will be studied via UV-vis, fluorescence spectroscopy and cyclic voltammetry. Light emission will be studied and tested in solution and in thin film form, before and after exposure to air and heat.

10:10 "Organic Solar Cells: A Sustainable Solution." Emily Orenstein (Undergraduate), Carroll College, Helena, MT, Muhammet Erkan Köse, Trent Anderson, Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND.

Organic solar cells use cheaper materials and less of these materials than silicon-based solar cells. Yet organic solar cells are much less efficient. Research is being done to examine what will increase the efficiency of organic solar devices. Through variation of deposition of the active layer, with the use of spin and spray techniques, the ideal bulk heterojunction morphology of organic photovoltaic devices was evaluated through measurement of power conversion efficiency, fill factor, open circuit voltage (Voc), short-circuit current density (Jsc) and charge mobility.

10:30 Break

10:45 "Comparing Nile Red and BODIPY in the Fluorescent Determination of the Lipid Content of Microalgae." John Kelly (Undergraduate), Doug Cameron. Montana Tech, Butte, MT.

Algae are one of the focuses in studies of potential sources for biofuels. Algae store energy in the form of either lipids or carbohydrates. Lipids can be used to make fuels such as biodiesel. The lipid content and composition are affected by the growing conditions of the algae and the algal species. Fluorescence spectroscopy is being investigated as a technique to determine total lipid content in (algae species). There are several different stains that can be used for determining lipid content in algae. The two being investigated here are Nile Red and BODIPY 505/515. They are being compared in terms of time, efficacy, and cost of lipid determination. Efficacy is evaluated by comparing the fluorescent methods to traditional gravimetric (solvent extraction) methods in terms of the total lipid content. The gravimetric methods are typically better methods for determining total lipid content but they are too slow to be used quickly in making a lipid content growth curve of the algae and they require much larger amounts of the algae as compared to the fluorescence methods. Removal of large amounts of algae from a growth experiment adversely affects the experiment.

11:05 "Novel G-quadruplex binders with a potential dual DNA cross-linking mechanism of action." Nathan S. Duncan (Graduate student), Alison K. Kearns and Nicholas R. Natale, University of Montana, Missoula, MT.

Genomic DNA, which is organized around double-stranded B-form DNA, is both durable and flexible enough to store and pass on genetic information. Once freed from the associations of an extended complimentary sequence, single stranded DNA and RNA can adopt a vast array of other stable secondary structure motifs, such as stem-loop, pseudo-knots, and tetra-loops, ideal for its involvement in other biological settings other than as a store of genetic information. Guanine-rich nucleic acids can fold into distinctive four-stranded conformers found in telomeric DNA repeats (i.e. TTAGGG), also known as G-quadruplexes (G4), as well as in sequences in the promoter and other regulatory regions of genes, especially those involved in cellular proliferation. Small molecules that induce the formation of, and/or selectively bind to, G-quadruplex structures are of interest for development as potential therapeutic agents, particularly in the anticancer therapeutic area. To date, quarfloxin is the only G-quadruplex ligand from the large number that has been developed to have progressed to clinical evaluation. Before their use in chemotherapy, alkylating agents were better known for their use as "mustard gas" and related chemical weapons in World War I. As such alkylating agents, in general, can react with one or two different 7-N-guanine residues and could potentially result in the cross-linkage of DNA strands, which prevents uncoiling of the DNA double helix leading to cell death. Novel 10-oxoanthracene derivatives were synthesized and characterized based on NMR studies. The synthesis, characterization, and biological studies will be presented.

11:25 "An Efficient and Scalable Extraction and Quantification Method for Algal Derived Biofuel." Egan J. Lohman (Graduate student), Robert D. Gardner, Luke Halverson, Richard Macur, Brent M. Peyton, Robin Gerlach. Department of Chemical and Biological Engineering, Montana State University, Bozeman, MT.

Microalgae are capable of synthesizing a multitude of compounds including biofuel precursors and other high value products such as omega-3-fatty acids. However, accurate analysis of the specific compounds produced by microalgae is important since slight variations in saturation and carbon chain length can affect the quality, and thus the value, of the end product. We present a method that allows for fast and reliable extraction of lipids and similar compounds from a range of algae, followed by their characterization using gas chromatographic analysis with a focus on biodiesel-relevant compounds. This method determines which range of biologically synthesized compounds is responsible for each fatty acid methyl ester (FAME); information that is fundamental for identifying preferred microalgae candidates as a biodiesel source. Traditional methods of analyzing these precursor molecules are time intensive and prone to high degrees of variation between species and experimental conditions. Here we detail a new method which uses microwave energy as a reliable, single-step cell disruption technique to extract lipids from live cultures of microalgae. After extractable lipid characterization (including lipid type (free fatty acids, mono-, di- or tri-acylglycerides) and carbon chain length determination) via GC-FID, the same lipid extracts are transesterified into FAME and directly compared to total biodiesel potential via GC-MS. This approach provides insight into the fraction of total FAME derived from extractable lipids compared to FAME derived from the residual fraction (i.e. membrane bound phospholipids, sterols, etc.). This approach can also indicate which extractable lipid compound, based on chain length and relative abundance, is responsible for each FAME. This method was tested on three species of microalgae; the marine diatom *Phaeodactylum tricornutum*, the model Chlorophyte *Chlamydomonas reinhardtii*, and the freshwater green alga *Chlorella vulgaris*. The method is shown to be robust, highly reproducible, and fast, allowing for multiple samples to be analyzed throughout the course of an experiment to provide time-

resolved information. Total time from harvest to obtaining analytical results is less than two hours.

Session B (Room 102)

9:10 "Mechanistic Insight of Radical AdoMet Enzyme HydG in [FeFe] Hydrogenase H-Cluster Maturation." Benjamin R. Duffus (Graduate student), Joan B. Broderick, John W. Peters, Ian R. Bruzas, Eric M. Shepard, and Shourjo Ghose**.** Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT.

Metalloenzymes are remarkable in catalyzing difficult chemical reactions under physiological conditions with transition metals at their active sites. The complex iron-sulfur (Fe-S) organometallic "H-cluster" cofactor from [FeFe]-hydrogenases catalyzes reversible proton reduction to yield dihydrogen at an active site comprised of a [4Fe-4S] cluster bridged to a 2Fe subcluster coordinated by a bridging dithiolate, two CN-, and three CO ligands. Biosynthesis of this cofactor is unique in its requirement for two radical S-adenosylmethionine (AdoMet) enzymes (HydG and HydE) with a scaffold GTPase (HydF). The radical AdoMet enzyme HydG has been shown to synthesize CO and CN-, together with p-cresol, through a radical-initiated fragmentation of the substrate tyrosine, using two bound [4Fe-4S] clusters. The N-terminal cysteine motif CX3CX2C binds the radical AdoMet [4Fe-4S], while the C-terminal CX2CX22C motif is unique to HydG. While the N-terminal cluster has precedent to initiate catalysis through generation of an AdoMet-derived 5'-deoxyadeonsyl radical, mechanistic insight to the role of the C-terminal cluster remains outstanding. Characterization of the C-terminal cluster has shown that it can coordinate a [4Fe-4S] cluster and that AdoMet does not perturb the cluster's electronic environment. Detected CO and CN- is exquisitely sensitive to the degree of intact cluster at both sites. The mechanistic implications of these observations provide a potential model for ligand biosynthesis and delivery to the immature 2Fe cluster.

9:30 "Alternative conformations of yeast iso-1-cytochrome c: effects of a gate keeping residue on heme crevice dynamics." Levi J. McClelland (Graduate student), Tung-Chung Mou, Margaret Jeakins-Cooley, Melisa M. Cherney, Ayesha Sharmin, Sandy Ross, Stephen Sprang, Bruce E. Bowler. Department of Biochemistry, The University of Montana, Missoula, MT.

Cytochrome c (Cytc) is a small, globular protein residing within the mitochondria that plays an important role in cellular energy production by facilitating electron transport. More recently, Cytc has been identified in initiating the caspase cascade leading to apoptosis, or programmed cell death, upon release from the mitochondria. Interaction of Cytc with CL on the mitochondrial membrane requires a loss of the native Met80 heme ligation. Loss of the native ligand enables cytochrome c to function as a peroxidase and oxidize CL. Cytc has a decreased affinity to oxidized CL, and can therefore be released from the membrane and the mitochondria propagating apoptosis. In order for the heme coordination site to open for peroxidase activity, the Ω-loop D of mitochondrial Cytc, one of the most conserved regions across all Cytc's, must undergo dynamic movement suggesting it may behave similarly to the alkaline conformational transition. In yeast wild-type iso-1- Cytc (yWT) a trimethylated lysine (TmLys) at residue 72 is

positioned near the heme crevice in contact with Thr78, Met80 and Ala81. We hypothesize that this steric interaction may act as a gatekeeper for the dynamic opening of the Ω-loop D enabling Met80 to swing outwards opening up the heme coordination site. A recent crystal structure of yeast iso-1- Cytc containing a TmLys72Ala mutation (WT*) demonstrates this open heme coordination site conformation with Met80 swung away from the heme. By placing an alanine at position 72 we are able to eliminate steric interactions originally present due to TmLys contacting Thr78, Met80 and Ala81. Using stopped-flow methods we can investigate the hypothesis that residue 72 may act as a gatekeeper of peroxidase activity by monitoring peroxidase activity in both the yWT and WT* variants. Furthermore, we also investigate the interaction of Cytc with CL nanodisc membranes. From these experiments we can gain an understanding of binding rates of Cytc to CL. Peroxidase activity and heme crevice dynamics when Cytc is bound to CL will also be determined. As it becomes important to understand the events leading to and propagating programmed cell death, it is important to understand the role of Cytc in apoptosis.

9:50 "Monitoring the Effects of Prickly Pear Antioxidants on Oxidatively Stressed Human Lung Cells Exposed to Chromium VI." Trace Forkan (Undergraduate), Katie Hailer and Michael Swimley. Montana Tech, Butte, MT.

Epidemiological studies have established the existence of an inverse correlation between the intake of phenolic-rich, or antioxidant containing, fruits and vegetables and the occurrence of various diseases, including cancer. In order to determine whether or not antioxidants of certain plants can counteract these reactions, the antioxidants extracted from a prickly pear plant will be incorporated into an existing culture of living, originally healthy, human lung cells which have been exposed to chromium VI that has resulted in oxidative stress. Human lung cells will be plated in a 96 well tissue culture plate, in which the appropriate wells are treated with antioxidant, chromium or control conditions and dichlorofluorescence (DCF) dye. The DCF dye is a dye sensitive to various types of oxidants and when measured with a fluorometer, will accurately measure the amount of oxidation occurring within the cells. Our study is a continuation of the same study previously conducted by Michael Swimley. This study is being conducted to gain additional data that helps statistically verifies Michael Swimley's results.

10:10 "Analyzing Chromium-Treated Human Lung Cells with Cranberry Antioxidants for Oxidative Damage." Micaul McClafferty (Undergraduate), Katie Hailer. Montana Tech, Butte, MT.

Chromate is a known carcinogen that causes oxidative damage and stress in cells. Cranberries contain phenols that could possibly decrease the level of oxidative damage, in turn decreasing the risk of cancer. The objective of this study is to test chromium-treated human lung cells, using the common carcinogen Cr (VI) to see if oxidative stress decreases with application of antioxidant extracts taken from either the leaf or stem of the *Mullica Queen* cranberry bush. The major phenolic acids identified in this species of cranberry are 3-caffeoylquinic acid and 5-caffeoylquinic acid. A cellular oxidative stress assay was performed to determine the antioxidant capabilities of the cranberry extracts. Human lung cells were grown and approximately 20,000 cells were plated in a 96-well plate. The cells were incubated for 48 hours, and then treated with either 12.5μM or 25μM chromium and antioxidants from either the leaf or the stem of the

cranberry. Dichlorofluorescence, a dye sensitive to a number of oxidants, was added to the cells after treatment, and then a fluorometer was used to determine oxidation levels. The preliminary results show that *Mullica Queen* antioxidants seem to decrease the amount of oxidative stress observed in the chromium-treated human lung cells.

10:30 Break

10:45 "**The Directed Encapsulation of a Hydrogenase within the P22 Capsid."** Paul Jordan (Graduate student), Trevor Douglas, Dustin P. Patterson, Kendall N. Saboda. Montana State University, Dept. of Chemistry & Biochemistry, Bozeman, MT.

The development of robust biobased catalysts integrated with large macromolecular assemblies, particularly those synthesized by biology represent an important area of biomaterials research. Virus capsids in particular are beautifully evolved examples of macromolecular containers for such catalysts. Our system exploits the capsid of the P22 bacteriophage from Salmonella typhimuriam which uses a scaffold protein (SP) to direct the assembly of 420 copies of the coat protein (CP) into a 58 nm icosahedral procapsid. Through the use of a truncated SP, genetic fusions of cargo to the SP have been engineered to package a wide array of gene products and catalytically active enzymes in the interior of the P22 capsid, to create new functionality. In this work, we have demonstrated the directed encapsulation of a [NiFe]-hydrogenase 1 from E. coli to the interior of the P22 (P22-Hyd). Importantly, the EcHyd-1 maintains its enzymatic activity through anaerobic protein purification, making it well-suited for materials applications. EcHyd-1 and other oxygen-tolerant [NiFe] hydrogenases are increasingly being used in biotechnology for their catalytic properties, including the uptake and evolution of molecular hydrogen, use of earth abundant metals (Fe, Ni), and oxygen tolerance. Recombinant over-expression of the large and small subunits of EcHyd-1 can lead to the assembly of an active EcHyd-1 utilizing the basal expression of the accessory proteins, found in the host E. coli, necessary for the assembly and maturation of the active sites. We have used this approach to achieve the encapsulation of an active hydrogenase inside the capsid of P22 using a temporal, differential expression of the components. This allows for maturation of the hydrogenase prior to packaging in the capsid and scaffold protein directed capsid assembly.

11:05 "Heat Treatment and Surfactant Exposure to the HEK 293 Cell Line to Induce Uptake of Metal Doped Hydroxyl Apatite Nanoparticles." Kelly McGrath (Undergraduate), Katie Hailer and Raj Kasinath. Montana Tech, Butte, MT.

HEK 293 cells were exposed to various metal-doped Hydroxyl apatite nanoparticle suspensions and supernatant along with EDTA in varying concentrations in a 96-well plate. This was done in an attempt to assess the possibility of cell death upon exposure to any of the given nanoparticles, or to the EDTA solvent. Cell viability was measured by a relationship to mitochondrial activity through the use of XTT, a dye that reacts with succinate dehydrogenase, producing a colorimetric form of XTT. Based on this, the activity of the mitochondria of the cells can be measured as a function of absorbance, recorded in 2 hour intervals in a 96 well-plate reader. These scans have only been conducted at 37°C thus far.

11:25 "Synthesis of DNA Methyltransferase Inhibitors." Ogar Ichire (Graduate student), Nigel Priestley. University of Montana, Missoula, MT.

DNA methylation and histone modification play a central role in epigenetic regulation of gene expression. DNA methyltransferase 1 (Dmnt1) is the most expressed DNA methyltransferase and is essential for maintaining methylation patterns during DNA replication and repair. Typically, DNA methylation occurs at the C5 position of cytosine almost exclusively in the CpG islands region, and over expression of DNMT1 has been associated with hypermethylation of the CpG islands. This uncontrolled hypermethylation pattern results in gene silencing if it occurs within the promoter region of the DNA, and such patterns have been observed in a number of cancerous cells. Thus, the development of DNMT1 inhibitors provides a novel opportunity for cancer therapy. Consequently, the current research project investigates the computational study and synthesis of isoindoline carboxamide analogs as potential inhibitors of DNMT1, and its application in slowing the growth of MCF-7 breast cancer cell line.

Session C (Room 112)

9:10 "Quantification of S mixing of dithiocarbamate ligands in transition metal complexes." Bradley Towey (Graduate student), Robert Szilagyi. Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT.

The molybdenum site of the iron-molybdenum cofactor (FeMo-co) of nitrogenase has been considered as one of the likely catalytic centers, where the stepwise biological reduction of dinitrogen to ammonia occurs. The $MoFe_3S_4(S_2CNEt2)_5$ cluster, which is a biomimetic model of FeMo-co, was synthesized in a one pot reaction. The determination of the electronic structure contribution of $[S_2CNEt_2]$- (dtc) ligands to the Mo-3Fe-4S cluster is under development using multi-edge X-ray absorption spectroscopy and density functional theory (DFT). To understand the contributions of these ligands, a series of model dtc complexes for the S K-edge were also synthesized. Transition dipole integrals for dtc ligands were developed from electron paramagnetic resonance data of $Cu(dtc)_2$. The experimental covalencies from the S K-edge of $M(dtc)_x$ (M=Cu(II), Ni(II), Fe(III) and Mo(IV), x=2,3,4) were determined and correlated with DFT. The contributions of dtc ligands can now be employed towards the elucidation of the total electronic structure of Mo-3Fe-4S biomimetic models of FeMo-co.

9:30 "Synthesis and Characterization of Au Nanoparticles Supports on Hybrids Inorganic/Polymeric Matrix for Chemioselective Chloronitrobencene Hydrogenation." Cristian H. Campos (Post-doc), Edward Rosenberg, Bruno F. Urbano, Bernabé L. Rivas, Cecilia C. Torres and Patricio A. Reyes. Dept of Chemistry & Biochemistry, University Of Montana, Missoula, MT.

This work reports the preparation of hybrids Inorganic/Polymeric composites using (4-vynilbenzyl) trimethylammonium chloride (ClVBTA) and three types of metal oxides (MxOy: Al_2O_3, TiO_2 and ZrO_2) using 3-(trimethoxysilyl)propilmethacrylate as compatibilizer in a radical

polymerization/sol-gel route synthesis. The composites were used as supports for syntheses of Au nanoparticles and characterized by FT-IR, XRD, ^{29}Si solid state NMR, S_{BET}, SEM and TGA techniques. The results indicate that all the materials were interpenetrating networks (IPN) and that the TMPM interacts forming bridges between the polymeric-inorganic networks. The yield of polymer phase with respect to the oxide shows that $Al_2O_3 > TiO_2 > ZrO_2$. The morphologies and the properties depend to the nature of the metal oxide incorporating in the network. All materials showed good thermal stability and typical morphologies for non-porous materials. The Au-composites has been rarely used in hydrogenation reactions because gold does not possess hydrogen chemisorption capacity. However, small gold particles behave differently and they may be able to chemisorb hydrogen to same extent, leading to possible activity in hydrogenation reactions. This may provide an advantage because this materials produce highly dispersed Au particles may be better controlled. Metallic nanoparticles were prepared by colloidal method using composites as reducing agent and stabilizer. The metal loading for all the metallic-composites was 0.5 wt%. The catalysts were then evaluated in the hydrogenation of *o, m* and *p*-nitrobenzene (x-NB) in a batch type reactor at 298K and 20 bar H_2 pressure. All the catalysts were active and ≥98% chemioselectives in the hydrogenation reaction.

9:50 "Truth and lies in equations of state for MgO." Reed A. Howald (Professor). Montana State University, Bozeman.

An equation of state embodied in a spreadsheet gives one access to all the thermodynamic properties of that material at all temperatures and pressures. This has been done for MgO for the best published equation of state, and for a new unpublished model that does better fitting known low temperature heat capacity and thermal expansion data. The independent variables for these spreadsheets are volume and temperature, so constant volume contour lines in P-T space are easily calculated. But other thermodynamic relationships like $C_p = (dH/dT)_p$ can be tested and illustrated.

Simple graphical representations of data and calculations can be misleading when large ranges are covered. The advantages of plotting $Q_1 = C_p/T^3$ versus T and $\alpha * B_T$ versus V are illustrated.

Even for an important substance like MgO there is very little accurate high pressure thermodynamic data available, and some method of extrapolation is essential. Since science is done by human beings, the choice of extrapolation methods is often unscientific.

10:10 "Development of Nickel-Ruthenium Catalyst on Composite Material." Sascha Stump (Research Assistant), Edward Rosenberg, Glenn Pinson. Department of Chemistry and Biochemistry. The University of Montana, Missoula, MT.

Current methods of producing hydrogen are expensive and cannot meet the growing demand for an alternative fuel source. We propose a hydrogenase mimic, consisting of an organometallic compound containing a nickel and ruthenium complex bound to a silica polyamine composite. In theory, the structure of the compound is such that the ruthenium complex may facilitate a two electron transfer through the nickel center to form a hydride. The hydride then may be able to find a free proton in solution and evolve hydrogen in the reduced form of H_2. The advantage of loading on a silica polyamine composite is the porous nature provides vast surface area for

catalysis and may improve the stability of the catalytic compound as well as providing a hydrophilic surface. The composite material anchor allows the catalyst to be heterogeneous. Currently our efforts are focused on the synthesis of the desired compound and anchoring it to the silica polyamine surface. The proposed compound consists of two cysteine molecules linked through their nitrogen atoms by an ethylene bridge. The ligand is then able to complex a nickel atom through the nitrogen and sulfur atoms contained in cysteine. The sulfur atoms additionally complex with a ruthenium atom bound to hexamethylbenzene, providing a source of electron density. The compound is anchored to the composite material through an amide bond with the carboxyl group on cysteine. The synthesized compound will be characterized as a hydride and the catalytic activity on and off the composite will be analyzed and compared.

10:30 Break

10:45 "Synthesis and Characterization of Fe-S Particle Clusters in Kaolinite." Emily Gravens (Undergraduate), R. Szilagyi. Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT.

This project explores the possibility of forming iron-sulfur particles in well-ordered clays such as kaolinite. Sulfur in the form of hydrogen sulfide (H_2S), was introduced anaerobically to three types of iron-enriched clays including kaolinite and a clay sample collected locally outside of Dillon, Montana. Samples were probed by X-ray Absorption Spectroscopy (XAS) to identify changes in electronic and geometric structures as a result of iron-doping and the formation of Fe-S particles in the presence of H_2S. Additionally, we show the first developments toward a computational approach for describing kaolinite. The model uses a cluster technique that is computationally inexpensive and would allow for taking advantage of common modeling techniques for molecular systems rather than using periodic boundary condition simulations. The proposed model will accurately describe the complete chemical system and predict the outcome of chemical reactions, particularly the intercalation of H_2S in natural and Fe-containing kaolinite. The combination of experimental and theoretical results lays the groundwork for more detailed studies that would assess catalytic activity of Fe-S clusters formed in clays.

11:05 "Multi-edge X-ray Absorption Near-edge Spectroscopic Analysis of Analogous Pd(II), Pd(III) and Pd(IV) Complexes." Rhonda Barton (Graduate student), Robert Szilagyi, Liviu Mirica. Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT.

Two consecutive one electron oxidations of the Pd^{II} complex, $^{Me}N_4Pd^{II}Cl_2$ (^{Me}N4= N,N'-dimethyl-2,11-diaza[3,3](2,6)pyridinophane), results in Pd(III) and Pd(IV) complexes with modified "^{Me}N4" ligand coordination[1]. The Pd(II) complex adopts a square planar geometry, with the pyridine nitrogens of the ^{Me}N4 ligand coordinating to the metal center. As the number of holes increases in the d manifold, the amine nitrogens of the ^{Me}N4 ligand coordinate at the axial positions of the complex in a pseudo octahedral fashion. This oxidation series of palladium complexes, novel in its unique use of ligand coordination, presents a rare and stable Pd(III) pre-catalyst for carbon bond coupling among the vast number of Pd(II) and Pd(IV) systems. These

three complexes will be characterized through multi-edge X-ray Absorption Near-Edge Spectroscopy (XANES), an element specific technique, which excites core electrons of the 1s and 2p orbitals to frontier molecular orbitals. Specifically, the chemical bonding of the Pd-Cl bonds and oxidation states of these complexes will be analyzed from multiple reference points from the Pd K-edge (Pd 1s), Cl K-edge (Cl 1s) and Pd L3-edge (Pd 2p J=3/2), providing a complementary picture of the electronic structures.

Mirica, L.M.; Khusnutdinova, J.R. Coord. Chem. Rev. 2013, *257*, 299.

11:25 "Synthesis and Characterization of PONOP Pincer Complexes on SPC." Md Abdul Goni, Edward Rosenberg. The University of Montana, Missoula, MT.

The metal complexes bound on polymers and on the surface-silanized silica gels could be utilized as attractive catalysts for various chemical transformations. This is because they are immobilized on the composite surface and the expensive catalytic complexes can easily be recovered for reuse through a simple filtration manipulation. Different metal PONOP pincer complexes have been synthesized on the silica polyamine composites to find their catalytic activity and also the impact of SPC surface on them. The pincer complexes have been constructed on the SPC surface stepwise. Three methods have been developed to load and synthesize the PONOP pincer ligand and the corresponding metal PONOP pincer complexes on the SPC. The synthesized metal pincer complexes on SPC have been characterized by ^{13}C and ^{31}P solid-state NMR as well as the elemental analysis techniques. Variation is found in the loading of different pincer complexes on SPC based on the three methods.

12:30 Keynote Address (Room 101)

Dr. Brent Peyton, Montana State University

Professor of Chemical and Biological Engineering
and Director of the Thermal Biology Institute

"Biological Diversity and Chemical Capability in Yellowstone Hot Springs"

Thermal ecosystems are relatively small, based on overall size and distribution across the planet, yet they maintain a significant and strategic role in the search for biocatalysts for novel processes. Hot springs are a natural ecosystem in which the microorganisms represent adaptation to elevated temperatures over centuries, making them a model environment for isolating relevant and robust microorganisms for biotechnology and energy applications. To date, thermal environments have been a source of beneficial microorganisms, including the discovery of microorganisms and thermostable enzymes (e.g., Taq polymerase), for the degradation of biomass, and the production of lipases, and for algal biofuels. This presentation will include results of interdisciplinary chemical and microbial investigations, and the characterization of unique microbes for enzyme discovery and biofuels applications.

Session D (Room 101)

1:30 "Structure Elucidation of an antitumor agent interaction with a quadruplex forming telomeric oligomer." Matthew J. Weaver (Graduate student), Earle Adams, Howard D. Beall, Alison K. Kearns, Philip Reigan and Nicholas R. Natale. The University of Montana, Missoula, MT.

Anthracenyl isoxazolyl amides (AIMs) have shown potent anti-tumor activity and now evidence for a novel mechanism of action has been visualized with the aid of solution nuclear magnetic resonance spectroscopy (NMR). G4 is specialized motif of DNA stabilized by a complex network of hydrogen bonds between guanine molecules.Human telomeric DNA of the sequence $(TTAGGG)_4$ has been studied by solution NMR and the formation of the unique G4 motif has been confirmed. This sequence of telomeric DNA forms a unimolecular quadruplex that is hypothesized to arise via the formation of a hairpin turn which subsequently folded in upon itself. One-dimensional NMR studies of the quadruplex have been performed to determine if interactions are present between G4 and AIMs, novel antitumor agents developed in our laboratory. Our preliminary results show *definitive magnetic anisotropy in the interaction of AIM with the telomeric oligomer*, direct evidence of the drug receptor interaction, and consistent with a π-stacking intermolecular complex. Due to the complexity of quadruplex structures one-dimensional experiments are insufficient. In order to probe the precise location and orientation of atom in the quadruplex structure higher order experiments were required. Nuclear overhauser effect spectroscopy (NOESY) experiments were used to obtain data which allows for the determination of the location of each hydrogen atom in the entire structure to be determined relative to the other hydrogen atoms. Data obtained from NOESY experiments is necessary to unambiguously assign the precise structure of the G-4-AIM interaction at atomic resolution, our progress regarding these experiments will be described.

1:50 "Isoxazolo[3,4-d]pyridazinones are positive modulators of the 7TM metabotropic glutamate receptors, and selective for subtypes 2 and 4." Christina Gates (Undergraduate), Yousef Mirzaei, Chris Koerner and Nicholas R. Natale. The University of Montana, Missoula, MT.

The seven transmembrane superfamily (7TM), also known as G-protein coupled receptors, GPCRs) is one of the largest superfamilies in the human genome, and with approximately 30% of marketed drugs targeting the 7TMs, this class of proteins is among the most successful among therapeutic targets. Each has a binding site which is called a Venus flytrap module (VFM) due to its shape. Isoxazolo[3,4-d]pyridazinones have been found previously to have both interesting biological activity and to work well as a precursor for medicinal chemistry synthesis. To make the isoxazolo[3,4-d]pyridazinones, an isoxazolyl-ketone was reacted with substituted hydrazines. These were tested at metabotropic glutamate receptors (mGluR) by the Psychoactive drug Screening Program of NIMH. The results showed that the series had positive activity only at mGluR2 and 4, predominantly at 4. From these data it appears that the isoxazolo[3,4-d]pyridazinones selectively bind to these particular receptors and lack cross-reactivity between them. This may imply that rather than binding at the VFM, the molecules may bind to another region, called an allosteric site, which varies for each receptor and helps to modulate each

receptor's activity. Interaction at mGluR4 receptor is important since it is a potential target for the treatment of Parkinson's disease. Our approach to the optimization of selectivity/activity is structure-based using binding to the allosteric site as the working hypothesis. A lipophilic group was attached to the molecule via a lateral metalation process or hydrazine addition, to access a potential second receptor space. The new synthesis and biological evaluation will be described.

Session E (Room 102)

1:30 "*In Aquo* Simulation of Bacterial Dehydrogenase Catalysis." Katie Burbank (Graduate student), Robert K Szilagyi. Montana State University, Dept. of Chemistry & Biochemistry, Bozeman, MT 59717.

A computational model that can accurately describe the interaction of the bioavailable form of high-valent uranium(VI) (uranyl or $[UO2]^{2+}$) with biomolecules is a powerful tool for providing atomic-scale quantum chemical description for a diverse set of experimental data. In this work, the performance of density functionals and basis sets, solvation models were evaluated in modeling $[UO2]^{2+}$ interactions with quinol-type cofactors of bacterial alcohol dehydrogenase.[1] We combined the most relevant experimental data for $[UO2]^{2+}$ coordination chemistry and quinol-type biological cofactors in order to develop a computational model that balances both accuracy and cost. With this model, we aim to understand the role that $[UO2]^{2+}$ plays in the inhibition of formaldehyde formation during bacterial dehydrogenase. Our first step is to look at the effect that weak interactions, found in our in aquo model, have on mechanistic calculations in comparison to work performed on methanol dehydrogenase with quinol-type cofactors found in the literature.[2]

1. VanEngelen, M. R.; Szilagyi, R. K.; Gerlach, R.; Lee, B. D.; Apel, W. A.; Peyton, B. M.: Environmental Science & Technology, 2011, 45(3), 937-942.
2. Leopoldini, M.; Russo, N.; Toscano, M.; Chem. Eur. J., 2007, 13, 2109-2117.

1:50 "The Study of Surface Bound Ruthenium Based Organometallic Probes and Controlling Luminescence and Lifetime Properties." Geoffrey Abbott (Graduate student), Robert Brooks, Edward Rosenberg, Michelle Terwilliger, Ayesha Sharmin. University of Montana, Missoula, MT.

Asymmetric ruthenium probes, have been shown to have long lifetimes and high quantum yields in solution compared to more symmetrical probes such as $[Ru(bpy)_3^{2+}][Cl^-]_2$. We have studied the effects that the binding of these probes to a surface has on their photophysical properties. This research has studied the effects that the surface, the particle size and number of anchor points have on both luminescence and the lifetimes of the probe. Through the study of a family of asymmetric Ru probes this work has shown that by varying different factors of a compound's binding to the surface of a silica particle changes in lifetime up to 8 fold can be achieved, as well as minor wavelength shifting. This opens the possibility for the creation of effective heterogeneous photocatalysts for such reactions as water splitting and many others.

Session F (Room 112)

1:30 "Electronic structure of[Ni(II)S4] complexes from S K-edgeX-ray absorption spectroscopy." Matt S. Queen (Graduate student), Bradley D. Towey, Kevin A. Murray, Brad S. Veldkamp, Harlan J. Byker, Robert K. Szilagyi. Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT.

Nickel complexes with S-containing ligands can manifest both classical/metal-based (innocent), or inverted/ligand-based, (non-innocent) behavior. Using sulfur K-edge X-ray absorption spectroscopy, we established a spectrochemical series for [Ni(II)SR4] complexes containing thiolate, aliphatic dithiolate, olefinic and aromatic enedithiolate, conjugated dithiocarboxylate, and aliphatic thioether ligands. In order to obtain quantitative S orbital compositions of the unoccupied frontier orbitals from XAS data, we developed a general method to estimate the S 1s→3p transition dipole integral for the above S-ligands by considering chemical shift in spectral features due to changes in the S effective nuclear charge among the ligands and as a result of binding to Ni. The XAS-based experimental orbital compositions are compared to a comprehensive set of density functional theory-based electronic structure calculations.

1:50 "Chemical and Mechanical Methods for the Prevention of Zinc Anode Passivation in Alkaline Electrolyte in Zinc-Air Fuel Cells." Laurel Sugden, Kristi Lindgren. Flathead Valley Community College, Kalispell, MT.

Metal-air fuel cells have the potential to become major energy storage solutions. Zinc is used in metal-air cells as an energy-dense, corrosion-resistant anode. The oxidation reaction that occurs at the surface of the zinc anode causes the eventual death of the cell due to the formation of a non-conducting surface film on the anode. Zinc oxide or possibly a mixture of oxides and carbonates is generally agreed to be responsible for this passivation of zinc anodes in potassium hydroxide electrolyte, and elimination of the layer has been vexing to the scientific community. In our research, we have developed an electrolyte flow system which eliminates any formation of a passivation layer on the anode, effectively immortalizing the cell. This mechanical system lent insight into the chemistry of anode passivation, but it may prove to be an impractical solution for some zinc-air applications, so a chemical solution is desirable. We are now experimenting with a variety of electrolyte additives to replicate the promising results of the mechanical setup. We expect this chemical approach to dramatically improve the efficiency of zinc use and the lifetime of these fuel cells with negligible increases in mass and volume.