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RPPR Final Report
as of 12-Oct-2022

Agency Code: 21XD

Proposal Number: 73493BB **Agreement Number: W911NF-19-1-0078**
INVESTIGATOR(S):

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Organization: **University of California - San Diego**
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Title: Molecular-Based Studies of Geochemical Interfaces in Complex Environments
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Report Term: 0-Other
Submitted By: Vicki Grassian Email: vhgrassian@ucsd.edu
Phone: (858) 534-2499

STEM Degrees: 6 **STEM Participants:** 9

Major Goals: The major goals of the project include:

Goal 1: to understand the transformation of chemical contaminants, such as industrial solvents and personal care products, on geochemical interfaces. These contaminants include monoethanolamine, 2-butoxyethanol and methyl ethyl ketone and represent a broad class of compounds that include amino alcohols, glycol ethers and ketones, respectively.

Goal 2: to probe and understand the behavior of biological components, oxyanions, and dissolved organic matter on geochemical interfaces in complex media. The purpose of this goal is to both interrogate the surface of geochemical interfaces with different biological components and to also go beyond “one at a time” component interactions that most studies investigate in order to build towards a more relevant, multi-component system bound in the environment. This will allow for us to begin to unravel the chemical complexity of competing surface species and the possible synergistic effects of multi-component systems.

Goal 3: to develop new micro-spectroscopic tools to investigate the chemistry occurring on geochemical interfaces. This goal is focused on investigating geochemical interfaces using spatially resolved molecular-based spectroscopic probes. This novel approach will be particularly useful in discerning the complex nature of adsorbate-surface interactions at geochemical interfaces in multi-component environments.

Accomplishments: For Goal 1, contaminants are found readily in water systems and can have a significant impact on the quality of those water systems and they can interact with geochemical surfaces and undergo transformation reactions, leading to the formation of other, potentially harmful, products. Thus, the aim of this goal is to study the surface chemistry of new contaminants and new surface chemistry using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy under different environmental conditions. Our focus in these studies was on monoethanolamine (MEA) a chemical contaminant found in urban environments and sourced from a variety of consumer products including cleaning agents and cosmetics. Although MEA has been extensively studied for carbon capture, there is little information about its interaction with geochemical interfaces. We investigate its pH dependent surface chemistry in this ARO-funded project. For the other two contaminants, 2-butoxyethanol and methyl ethyl ketone we saw little interaction.
In our studies, MEA adsorption on titanium dioxide as a function of pH that demonstrated adsorption is a highly pH dependent process and that electrostatic interactions dominate that process. We have also done experiments that probed MEA adsorption on hematite (α-Fe2O3) nanoparticles as a function of pH. Our results indicate that like adsorption on TiO2, MEA has the greatest adsorption on α-Fe2O3 at pH 10. To observe how other environmental

affected MEA adsorption on both oxide surfaces, adsorption experiments were performed across a range of solution concentrations and ionic strengths at pH 10 (since adsorption is greatest at this pH). Concentration results show that MEA adsorption increases linearly at lower concentration and then leveling off as the concentration was increased, suggesting Langmuir-like adsorption. This study was published in 2022 in the Journal of Colloid and Interface Science.

For Goal 2, biomolecules play essential roles in many environmental and biological processes. Adsorbed biomolecules can affect particle physicochemical properties, influencing fate and transport. Moreover, the presence of multiple components in environmental and biological systems presents a complex scenario in which there can be competitive adsorption and synergistic interactions between adsorbates. When biomolecules interact with geochemical surfaces (e.g., TiO_2 or Fe_2O_3 nanoparticles) in environmental and biological aqueous milieu, they can adsorb, forming a dynamic structure at the interface. The fate of biomolecules in the environment depends in part on understanding the surface chemistry occurring at the biological-geochemical (bio-geo) interface. Interestingly, little is known about how environmental DNA (eDNA) or smaller component oligonucleotides and nucleotides persist in aquatic environments and the role of surface interactions. In this ARO funded project, we probed surface interactions and adsorption behavior of nucleotides on oxide surfaces. We have investigated the interactions of individual nucleotides (dGMP, dCMP, dAMP, and dTMP) on TiO_2 particle surfaces as a function of pH and in the presence of complementary and noncomplementary base pairs. Using attenuated total reflectance-Fourier transform infrared spectroscopy and UV/Vis spectroscopy, there was an increase in the coverage of adsorbed nucleotides at lower pH with nucleotides interacting with the oxide surface via the phosphate group. Additionally, differential adsorption behavior was seen with purine nucleotides over their pyrimidine derivatives with purine nucleotides being preferentially adsorbed and with higher surface saturation coverage. These differences may be a result of intermolecular interactions between co-adsorbed nucleotides. When the TiO_2 surface was exposed to two component solutions of nucleotides, there was preferential adsorption of dGMP compared to dCMP and dTMP, and dAMP compared to dTMP and dCMP. Complementary nucleotide base pairs showed hydrogen-bond interactions between a strongly adsorbed nucleotide layer and weaker interacting hydrogen-bonded second layer. Noncomplementary base pairs did not form a second layer. These results highlight several important findings: (i) there is differential adsorption of nucleotides; (ii) complementary co-adsorbed nucleotides show base pairing with a second layer and the stability depends on the strength of the hydrogen bonding interactions and; (iii) the first layer coverage strongly depends on pH. Overall, the importance of surface interactions in the adsorption of nucleotides and the templating of specific interactions between nucleotides have been shown.

To develop a more comprehensive suite of nucleotide adsorption onto other mineral surfaces. We investigated the interaction of different iron-containing minerals with the four nucleotides, For all four nucleotides and regardless of nanoparticle composition, the phosphate group was seen to broaden and undergo significant peak shifting. When the four adsorbed hematite spectra are compared, the phosphate bands peak position and broadening are similar. This suggests that the complexation modes of all four nucleotides bound to hematite, are identical. For goethite, the phosphate peak shift and broadening are similar for all four nucleotides. Overall, the surface chemistry on hematite and goethite are composed of different mixtures of complexation modes and are independent of the ribose and purine or pyrimidine rings. We have engaged with computational chemists to better understand the interactions of different nucleotides especially as it relates to differences in the attachment to different mineral surfaces.

Adsorption of more complex biomolecules impacts both particle physicochemical properties and sorbate reactivity and transport, as conformation and active sites change during complexation. Retention of biomolecules at an interface is, however, complicated by the heterogeneity of environmental and biological matrices. We have investigated adsorption kinetics, coverage, and conformation of two ubiquitous proteins, β-lactoglobulin (β-LG) and bovine serum albumin (BSA) onto hematite (α-Fe_2O_3) in the presence and absence of oxyanion phosphate. These results show dynamic changes in the secondary structures of both proteins when adsorbed onto nanoscale α-Fe_2O_3 surfaces, compared to their unbound conformations. However, these differences were attenuated in the presence of adsorbed phosphate. Overall, these results reveal the importance of phosphate on protein-mineral adsorption kinetics and conformation, a critical driver of protein function, in complex aqueous systems and expands our understanding of biomolecule-geochemical surface interactions in multi-component systems. We published a paper in Environmental Science:Nano on this work.

For Goal 3, atomic force microscopy-infrared (AFM-IR) spectroscopy was further developed to probe adsorbate-surface interactions on geochemical interfaces. We have further investigated the interaction of Suwannee River Fulvic Acid (SRFA), a commonly used model fraction of natural organic matter, with α-FeOOH particle surfaces. AFM imaging and IR spectra taken on SRFA thin films at various pH values indicated the highly heterogenous nature of these samples. We have also investigated biological components. Overall this has been an important breakthrough in the vibrational analysis of complex environmental samples.

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Training Opportunities: Students involved in these projects have progressed in both their academic research and professional careers while developing skills that require a deep understanding of technical and theoretical knowledge. Moreover, the interdisciplinary nature of Goals 1-3 has also helped build networks and improve interpersonal skills between colleagues. Senior graduate students have taught and assisted with experimental designs, data analysis and manuscript preparation related to Goals 1-3. Furthermore, undergraduate researchers have been involved in these projects to help encompass the development of soft and hard technical skills such as, interdisciplinary collaboration, communication, experimental independence, and result dissemination through presentations. Goal 2 required nucleotide separation and quantification which required training and usage of an the Thermo Scientific Vanquish Flex Ultra-High performance liquid chromatography in an NSF funded facility in UCSD, Environmental and Complex Analysis Laboratory. Goal 3 involved paving the way for future studies of micro and nanoscale vibrational analyses of complex environmental samples.

Results Dissemination: Over the time frame of this grant, the PI and students presented research talks and posters on this project. For the PI, during at least half of the time the grant was active presentations occurred on zoom including: University of Rochester Department of Chemical Engineering; National American Chemical Society Spring 2021; National American Chemical Society Fall 2021; German Physical Society Surface Science Division 2021; UC Berkeley student-invited seminar 2020. In person presentations occurred at ACS Spring meeting in San Diego.
A graduate student is scheduled to give an oral presentation at the 2021 International Chemical Congress of Pacific Basin Societies in December 2021 to report results from Goal 2, this ended up being a zoom event. An undergraduate gave several oral presentations reporting Goal 2 results to the scientific community as well as the general public. Specifically at the University of California, San Diego Undergraduate Research Conference and Undergraduate Research Symposium.
Several publications are published or being worked on by the students involved in the project.
Sit, I.; Sagisaka, S.; Grassian, V. H. “Nucleotide Adsorption on Iron (III) Oxide Nanoparticle Surfaces: Insights into Nano-Geo-Bio Interactions Through Vibrational Spectroscopy” Langmuir 2020, 36, 15501?15513.
Sit, I.; Wu, H.; Grassian, V. H. “Environmental Aspects of Oxide Nanoparticles: Probing Oxide Nanoparticle Surface Processes Under Different Environmental Conditions” Annual Reviews of Analytical Chemistry 2021, 14, 489 – 514.

Ustunol, I., Coward, E. K., Quirk, E., Grassian, V. H., “Interaction of Beta-Lactoglobulin and Bovine Serum Albumin with Iron Oxide (?-Fe2O3) Nanoparticles in the Presence and Absence of Pre-Adsorbed Phosphate” Environmental Science:Nano 2021, 8, 2811-2823.

Ustunol, I., Metal Oxide Nanoparticles in Complex Environments: Characterization, Implications, and Biomolecule-Nanoparticle Interactions. PhD Dissertation, University of California, San Diego, La Jolla, CA 2021
Rose, A.; Hettiarachchi, E.; Grassian Grassian, V. H., Surface Chemistry of Monoethanolamine on Oxide Surfaces, Journal of Colloid and Interface Science 2022, 614, 75-83.
Kim, D.; Grassian, V. H., “ATR-FTIR and AFM-IR Spectroscopic Investigation of Suwannee River Fulvic Acid and Its Interactions with ?–FeOOH” ACS Earth and Space Chemistry 2022, 6, 81–89.

Sit, I. “Spectroscopic Measurements of Oxide Nanoparticles as a Probe of Nanoparticle-Biological Interactions and Nanoconfinement” PhD Dissertation, University of California, San Diego, La Jolla, CA 2022

Sit, I.; Quirk, E.; Grassian, V. H., “Differential Surface Interactions and Surface Templating of Nucleotides (dGMP, dCMP, dAMP and dTMP) on Oxide Particle Surfaces” 2022 Revised manuscript in review in Langmuir

Bañuelos, J. L.; Borguet, E. U.; Brown, G. E.; Cygan, R. T.; DeYoreo, J. J. Dove, P. M.; Gaigeot, M.-P.; Geiger, F. M.; Gibbs, J. M.; Grassian, V. H.; Ilgen, A. G.; Jun, Y.-S.; Kabengi, N.; Katz, L.; Kubicki, J. D.; Lu?tzenkirchen, J.; Putnis, C.V.; Remsing, R. C.; Rosso, K. M.; Rother, G.; Sulpizi, M.; Villalobos, M.; Zhang, H. “Oxide- and Silicate-Water Interfaces and Their Roles in Technology and the Environment” 2022 revised manuscript in review at Chemical Reviews.

Kim, D.; Grassian, V. H., Nanoscale Heterogeneities within Thin Films of Proteins, Oxyanions, and Goethite, 2022 submitted to Analytical Measurements

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Honors and Awards: PI and co-PI:
Vicki Grassian
2023 ACS Geochemistry Division Medal Award
2022 Sustainable Nanotechnology Organization “Tribute to Vicki Grassian” Session
2021 American Chemical Society National Award in Surface Chemistry
2021 NSF Distinguished Lecturer in Mathematical and Physical Sciences
2020 Sustainable Nanotechnology Organization Award
2020 American Academy of Arts and Sciences, Elected Member
2020 Iota Sigma Pi National Honorary Member
2019 Nichols Medal Award
2019 IUPAC Distinguished Women in Chemistry and Chemical Engineering Awardee
2019 Inclusive Excellence Award, UC San Diego

Wei Xiong
2019 NSF CAREER Award
2019 ACS JPC/PHYS Lectureship Award
2020 Sloan Research Fellow
2020 NIH Maximizing Investigator's Research Award (MIRA)

Graduate and Undergraduate awards
Eleanor Quirk – received a 2021 Future of Chemistry Scholarship for Women, provided by The Chemours Company. Eleanor Quirk also received a TREL award in Spring 2021.
Deborah Kim – 2021 Department of Chemistry & Biochemistry Equity, Diversity, Inclusion and Climate award
Deborah Kim– NSF GRFP 2020 Honorary mention
Izaac Sit – Best Poster Award, Pan-American Nanotechnology Conference 2020, São Paulo, Brazil
Izaac Sit – Travel Award, Pan-American Nanotechnology Conference 2020, São Paulo, Brazil
Irem B. Ustunol – Travel Award, Pan-American Nanotechnology Conference 2020, São Paulo, Brazil
Irem B. Ustunol – Student Award, 8th Sustainable Nanotechnology Organization Conference 2019, San Diego, CA, USA
2019 Haotian Chen, Undergraduate Student, 2019 Mayer Award

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Elizabeth Coward
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Co PD/PI
Participant: Wei Xiong
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Izaac Sit
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:

National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Deborah Kim
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Irem Ustunol
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Amber Rose
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Stacy Liang
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Carlos Diaz
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Haotian Chen
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Eleanor Quirk
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Sayuri Sagisaka
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: PD/PI
Participant: Vicki Grassian
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Eshani Hettiarachchi
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

ARTICLES:

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Date Submitted: 8/19/21 12:00AM Date Published: 12/2/20 12:00AM
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Article Title: Nucleotide Adsorption on Iron(III) Oxide Nanoparticle Surfaces: Insights into Nano–Geo–Bio Interactions Through Vibrational Spectroscopy
Authors: Izaac Sit, Sayuri Sagisaka, Vicki H. Grassian
Keywords: geochemical interfaces, nanoparticles, nano-bio interactions, hematite, nucleotide adsorption
Abstract: Surface chemistry affects the physiochemical properties of nanoparticles in a variety of ways. Therefore, there is great interest in understanding how nanoparticle surfaces evolve under different environmental conditions of pH and temperature. Here, we discuss the use of vibrational spectroscopy as a tool that allows for in situ observations of oxide nanoparticle surfaces and their evolution due to different surface processes. We highlight oxide nanoparticle surface chemistry, either engineered anthropogenic or naturally occurring geochemical nanoparticles, in complex media, with a focus on the impact of (a) pH on adsorption, intermolecular interactions, and conformational changes; (b) surface coatings and coadsorbates on protein adsorption kinetics and protein conformation; (c) surface adsorption on the temperature dependence of protein structure phase changes; and (d) the use of two-dimensional correlation spectroscopy to analyze spectroscopic results for complex systems. An outlook
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Date Submitted: 8/19/21 12:00AM Date Published: 6/1/21 7:00AM
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Article Title: Environmental Aspects of Oxide Nanoparticles: Probing Oxide Nanoparticle Surface Processes Under Different Environmental Conditions
Authors: Izaac Sit, Haibin Wu, Vicki H. Grassian
Keywords: surface displacement, ATR-FTIR spectroscopy, 2DCOS, eDNA adsorption, protein adsorption and structure, nucleotide adsorption, environmental synergistic effects
Abstract: Surface chemistry affects the physiochemical properties of nanoparticles in a variety of ways. Therefore, there is great interest in understanding how nanoparticle surfaces evolve under different environmental conditions of pH and temperature. Here, we discuss the use of vibrational spectroscopy as a tool that allows for in situ observations of oxide nanoparticle surfaces and their evolution due to different surface processes. We highlight oxide nanoparticle surface chemistry, either engineered anthropogenic or naturally occurring geochemical nanoparticles, in complex media, with a focus on the impact of (a) pH on adsorption, intermolecular interactions, and conformational changes; (b) surface coatings and coadsorbates on protein adsorption kinetics and protein conformation; (c) surface adsorption on the temperature dependence of protein structure phase changes; and (d) the use of two-dimensional correlation spectroscopy to analyze spectroscopic results for complex systems. An outlook
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Article Title: ATR-FTIR and AFM-IR Spectroscopic Investigation of Suwannee River Fulvic Acid and Its Interactions with alpha–FeOOH
Authors: Deborah Kim, Vicki Grassian
Keywords: geochemical interfaces, dissolved organic matter, nanoscopic imaging and spectroscopy
Abstract: Chemical contaminants are becoming an increasingly greater concern for water quality and it is well known that interactions with geochemical interfaces impact the fate and transport of these contaminants in the environment. In this study, we investigated the interactions of one such chemical contaminant, monoethanolamine (MEA), with oxide surfaces, particularly titanium dioxide (TiO2) and iron oxide (?-Fe2O3). Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy was used to probe the adsorption behavior of MEA on titanium dioxide (TiO2) and iron oxide (?-Fe2O3) nanoparticles as a function of pH and other environmental conditions including concentration and ionic strength. Overall, this study provides important insights into the surface chemistry and interactions between an alkanolamine and geochemical oxide interfaces.
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Article Title: Monoethanolamine Adsorption on Oxide Surfaces
Authors: Amber Rose, Eshani Hetttiarachchi, Vicki Grassian
Keywords: surface chemistry, chemical contaminants, monoethanolamine, geochemical interfaces, Attenuated Total Reflectance Fourier Transform Infrared spectroscopy, pH and environmental conditions.
Abstract: Chemical contaminants are becoming an increasingly greater concern for water quality and it is well known that interactions with geochemical interfaces impact the fate and transport of these contaminants in the environment. In this study, we investigated the interactions of one such chemical contaminant, monoethanolamine (MEA), with oxide surfaces, particularly titanium dioxide (TiO2) and iron oxide (?-Fe2O3). Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy was used to probe the adsorption behavior of MEA on titanium dioxide (TiO2) and iron oxide (?-Fe2O3) nanoparticles as a function of pH and other environmental conditions including concentration and ionic strength. Overall, this study provides important insights into the surface chemistry and interactions between an alkanolamine and geochemical oxide interfaces.
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Article Title: Interaction of Beta-Lactoglobulin and Bovine Serum Albumin with Iron Oxide (?-Fe2O3) Nanoparticles in the Presence and Absence of Pre-Adsorbed Phosphate
Authors: Irem Ustunol, Elizabeth Coward, Eleanor Quirk, Vicki Grassian
Keywords: Protein adsorption, iron oxide nanoparticles, nano-bio interactions, ATR-FTIR, phosphate.
Abstract: Protein adsorption onto mineral nanoparticle surfaces is critical to the function and fate of biological compounds in environmental and industrial systems. However, adsorption kinetics, coverage, and conformation of biological macromolecules are poorly understood, particularly in the presence of ubiquitous oxyanions. In this study, the adsorption of two proteins, beta-lactoglobulin (?-LG) and bovine serum albumin (BSA), onto hematite (?-Fe2O3) nanoparticles was investigated in the presence and absence of pre-adsorbed phosphate. Using solution and temporal solid-phase attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, our results show dynamic changes in the secondary structures of both proteins when adsorbed onto nanoscale ?-Fe2O3 surfaces, compared to their unbound conformations. However, these differences were attenuated in the presence of adsorbed phosphate. Adsorbed phosphate significantly reduced the protein surface coverage on iron oxide nanoparticle
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Article Title: Differential Surface Interactions and Surface Templating of Nucleotides (dGMP, dCMP, dAMP and dTMP) on Oxide Particle Surfaces
Authors: Izaac Sit, Eleanor Quirk, Vicki Grassian
Keywords: nucleotides, adsorption, geo-interfaces,
Abstract: The fate of biomolecules in the environment depends in part on understanding the surface chemistry occurring at the biological-geochemical (bio-geo) interface. Little is known about how environmental DNA (eDNA) or smaller component oligonucleotides and nucleotides persist in aquatic environments and the role of surface interactions. This study aims to probe surface interactions and adsorption behavior of nucleotides on oxide surfaces. We have investigated the interactions of individual nucleotides (dGMP, dCMP, dAMP and dTMP) on TiO2 particle surfaces as a function of pH and in the presence of complementary and noncomplementary base pairs. These results highlight several important findings: (i) there is differential adsorption of nucleotides; (ii) complementary co-adsorbed nucleotides show base pairing with a second layer and the stability depends on the strength of the hydrogen bonding interactions and; (iii) the first layer coverage strongly depends on pH.
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Authors: Deborah Kim, Vicki Grassian
Keywords: nanoscale heterogeneities, AFM-PTIR spectroscopy, environmental films, geochemical interfaces
Abstract: Minerals in groundwater interact with various chemical and biological species including organic matter, proteins, and prevalent oxyanions resulting in surface coatings and thin films of these different components. Surface interactions and the surface adsorption of these components on both oxide and oxyhydroxide iron surfaces have been widely investigated using a variety of spectroscopic methods. Despite these numerous studies, there still remains uncertainty with respect to interactions between these individual components, as well as heterogeneities and phase segregations within these thin films. In this study, we investigate mixtures containing Fe-containing minerals, proteins, and oxyanions to better understand surface interactions and phase segregation, AFM-PTIR spectroscopy can identify both nano- and microscale heterogeneities present within these thin films that are due to phase segregation and mineral surface interactions.
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Authors: José Bañuelos, Eric Borguet, Gordon Brown, Randall Cygan, James DeYoreo, Patricia Dove, Marie-Pie
Keywords: oxide interfaces, structure and dynamics, adsorption and reactions, dissolution and precipitation, environment, technology
Abstract: Interfacial reactions drive all elemental cycling on Earth and play a pivotal role in human life such as agriculture, water purification, energy production, environmental contaminant remediation, and nuclear waste repository management. Chemistry at such interfaces has been a focus of research for several decades, with the most recent comprehensive review published in 1999 (Brown et al., Chemical Reviews). Here we critically review research advances on structure, reactivity, and dynamic and coupled processes at oxide- and silicate-water interfaces in the last 20+ years and discuss the future opportunities. This critical review discusses how science is progressing from understanding the ideal oxide- and silicate-water interfaces to more realistic systems, focusing on accomplishments in the last 20 years, and identifying the remaining unknowns, outstanding challenges, and future opportunities for the community to address and/or to seek in the decades to come.
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Paper Title: AFM-IR and SFG Analysis on Various Geochemical Interfaces with Adsorbed BSA
Authors: Deborah Kim. Haotian Chen, Wei Xiong, Vicki Grassian
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Conference Name: ACS Fall 2019 National Meeting and Exposition
Date Received: 10-Aug-2020 Conference Date: 25-Aug-2019 Date Published: 29-Aug-2019
Conference Location: San Diego Convention Center, San Diego, CA
Paper Title: Investigation of Monoethanolamine Adsorption on Titanium Dioxide
Authors: Amber Rose, Izaac Sit and Vicki Grassian
Acknowledged Federal Support: **Y**

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Date Received: 11-Aug-2020 Conference Date: 25-Aug-2019 Date Published: 29-Aug-2019
Conference Location: San Diego Convention Center, San Diego, CA
Paper Title: DNA adsorption on iron (III) oxide: Effects of pH and ionic strength on surface interactions
Authors: Isaac Sit, Vicki Grassian
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: Sustainable Nanotechnology Organization Meeting
Date Received: 11-Aug-2020 Conference Date: 07-Nov-2019 Date Published: 09-Nov-2019
Conference Location: Bahia Resort Hotel, San Diego, CA
Paper Title: Nucleotide Adsorption on Iron (III) Oxide Nanoparticle Surfaces: Effects of pH and Co-adsorbates
Authors: Izaac Sit, Sayuri Sagisaka, Vicki Grassian
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: Pan-American Nanotechnology
Date Received: 11-Aug-2020 Conference Date: 04-Mar-2020 Date Published: 07-Mar-2020
Conference Location: Aguas de Lindoia, Sao Paulo, Brazil
Paper Title: Nucleotide Adsorption on Iron (III) Oxide Nanoparticle Surfaces: Effects of pH, Co-adsorbates, and Ionic Strength
Authors: Izaac Sit, Sayuri Sagisaka, Vicki Grassian
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: Pan-American Nanotechnology Conference
Date Received: 11-Aug-2020 Conference Date: 04-Mar-2020 Date Published: 07-Mar-2020
Conference Location: Aguas de Lindoia, Sao Paulo, Brazil
Paper Title: Effects of Phosphate on Protein-Nanoparticle Surface InteractionsU
Authors: Irem Ustunol, Vicki Grassian
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: Pan-American Nanotechnology Conference
Date Received: 11-Aug-2020 Conference Date: 04-Mar-2020 Date Published: 07-Mar-2020
Conference Location: Aguas de Lindoia, Sao Paulo, Brazil
Paper Title: Effects of Phosphate on Protein-Nanoparticle Surface Interactions
Authors: Irem Ustunol, Vicki Grassian
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: National American Chemical Society Meeting - San Antonio
Date Received: 06-Oct-2022 Conference Date: 13-Aug-2021 Date Published:
Conference Location: San Antonio
Paper Title: Interfacial reactions involving thin films of particles
Authors: Vicki Grassian
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: National American Chemical Society Meeting in San Diego
Date Received: 06-Oct-2022 Conference Date: 22-Mar-2022 Date Published:
Conference Location: San Diego
Paper Title: AFM-IR spectroscopy as a tool to probe micro and nanoscale heterogeneities within environmental films containing organic matter, biological components, oxyanions, and minerals
Authors: Deborah Kim, Vicki Grassian
Acknowledged Federal Support: **Y**

DISSERTATIONS:

RPPR Final Report
as of 12-Oct-2022

Publication Type: Thesis or Dissertation
Institution: University of California San Diego
Date Received: 06-Oct-2022 Completion Date: 1/26/21 4:32PM
Title: Metal Oxide Nanoparticles in Complex Environments: Characterization, Implications, and Biomolecule-Nanoparticle Interactions
Authors: Irem Ustulo
Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation
Institution: University of California San Diego
Date Received: 06-Oct-2022 Completion Date: 11/18/22 8:00AM
Title: Spectroscopic Measurements of Oxide Nanoparticles as a Probe of Nanoparticle-Biological Interactions and Nanoconfinement
Authors: Isaac Sit
Acknowledged Federal Support: **Y**

Partners

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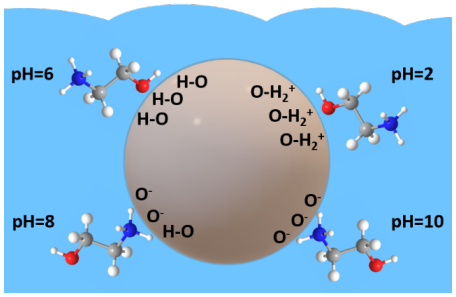
I certify that the information in the report is complete and accurate:
Signature: Vicki H Grassian
Signature Date: 10/6/22 4:29PM

Full Abstracts of Publications with TOCs/Representative Figures

Monoethanolamine Adsorption on Oxide Surfaces

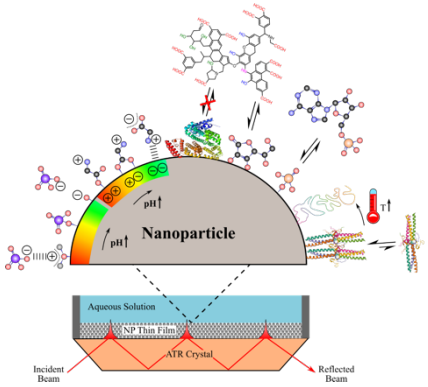
Amber N. Rose, Eshani Hettiarachchi, and Vicki H. Grassian (*published in JC IS*)



Abstract. Chemical contaminants are becoming an increasingly greater concern for water quality and it is well known that interactions with geochemical interfaces impact the fate and transport of these contaminants in the environment. In this study, we investigated the interactions of one such chemical contaminant, monoethanolamine (MEA), with oxide surfaces, particularly titanium dioxide (TiO_2) and iron oxide (α-Fe_2O_3). Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy was used to probe the adsorption behavior of MEA molecules on titanium dioxide (TiO_2) and iron oxide (α-Fe_2O_3) nanoparticles as a function of pH and other environmental conditions including concentration, and ionic strength. Both the extent and initial rates of adsorption of MEA molecules on these oxide surfaces increased with increasing pH. Adsorption on these oxide surfaces increases with solution concentration until saturation occurs and MEA adsorbs more readily at higher pH. Furthermore, adsorption decreases with increasing ionic strength, demonstrating the importance of electrostatic interactions to this process. Based on these results, a mechanistic picture emerges for the interaction of MEA with titanium dioxide and iron oxide across a range of pH values. Overall, this study provides important insights into the surface chemistry and interactions between an alkanolamine and geochemical oxide interfaces.

Environmental Aspects of Oxide Nanoparticles: Probing Oxide Nanoparticle Surface Processes Under Different Environmental Conditions

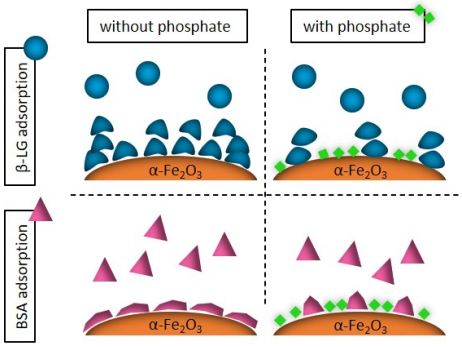
Izaac Sit, Haibin Wu and Vicki H. Grassian (published in *Annual Reviews of Analytical Chemistry*)



Abstract. Surface chemistry affects the physiochemical properties of nanoparticles in a variety of ways, therefore, there is great interest in understanding how nanoparticle surfaces evolve under different environmental conditions of pH and temperature. Here we discuss the use of vibrational spectroscopy as a tool that allows for *in-situ* observations of oxide nanoparticle surfaces and their evolution due to different surface processes. We highlight oxide nanoparticle surface chemistry, either engineered or naturally occurring geochemical nanoparticles, in complex media with a focus on the impact of: (1) pH on adsorption, intermolecular interactions and conformational changes; (2) surface coatings and co-adsorbates on protein adsorption kinetics and protein conformation and; (3) surface adsorption on the temperature dependence of protein structure phase changes; and (4) the use of two-dimensional correlation spectroscopy to analyze spectroscopic results for complex systems. An outlook of the field and remaining challenges is presented towards the end of this review.

Interaction of Beta-Lactoglobulin and Bovine Serum Albumin with Iron Oxide (α-Fe_2O_3) Nanoparticles in the Presence and Absence of Pre-Adsorbed Phosphate

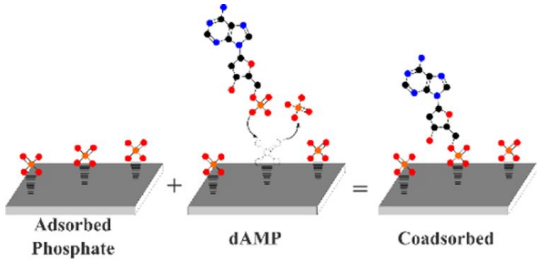
Irem B. Ustunol, Elizabeth K. Coward, Eleanor Quirk, and Vicki H. Grassian (published in *ES:Nano*)



Abstract. Protein adsorption onto mineral nanoparticle surfaces is critical to the function and fate of biological compounds in environmental and industrial systems. However, adsorption kinetics, coverage, and conformation of biological macromolecules are poorly understood, particularly in the presence of ubiquitous oxyanions. In this study, the adsorption of two proteins, beta-lactoglobulin (β-LG) and bovine serum albumin (BSA), onto hematite (α-Fe_2O_3) nanoparticles was investigated in the presence and absence of pre-adsorbed phosphate. Using solution and temporal solid-phase attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, our results show dynamic changes in the secondary structures of both proteins when adsorbed onto nanoscale α-Fe_2O_3 surfaces, compared to their unbound conformations. However, these differences were attenuated in the presence of adsorbed phosphate. Adsorbed phosphate significantly reduced the protein surface coverage on iron oxide nanoparticle surfaces, and impacted protein adsorption kinetics. The latter was observed to be protein-specific, with β-LG exhibiting a higher adsorption rate and sigmoidal kinetics compared to slower, more Langmuir-type kinetics of BSA adsorption. Our results reveal the importance of phosphate on protein-mineral adsorption kinetics and conformation, a critical driver of protein function, in complex environmental systems.

Nucleotide Adsorption on Iron (III) Oxide Nanoparticle Surfaces: Insights into Nano-Geo-Bio Interactions Through Vibrational Spectroscopy

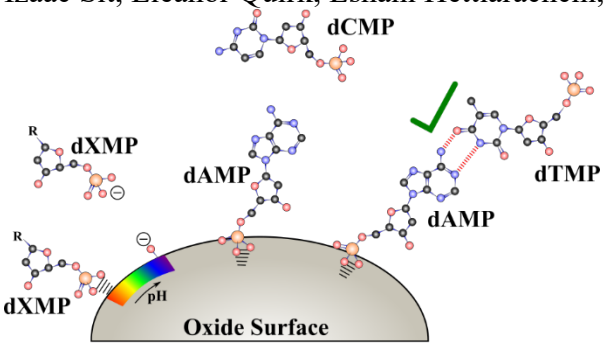
Izaac Sit, Sayuri Sagisaka, Vicki H. Grassian (published in *Langmuir*)



Abstract. Molecular processes at geochemical interfaces impact many environmental processes that are critical to the fate and transport of contaminants in water systems. Often these interfaces are coated with natural organic matter, oxyanions, or biological components, yet little is understood about these coatings. Herein, we are interested in better understanding the interaction of biological components with nanoscale iron oxide minerals. In particular, we use attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to investigate the adsorption behavior of deoxyadenosine monophosphate (dAMP) on hematite nanoparticle surfaces as a function of pH and in the presence and absence of adsorbed phosphate. These results show that fewer nucleotides adsorb at higher pH. Additionally, when phosphate anions are pre-adsorbed, nucleotide adsorption is significantly limited due to site-blocking by adsorbed inorganic phosphate. The pH dependence provides insights into the adsorption process and the importance of electrostatic interactions. Pre-adsorbed phosphate affects the binding mode of dAMP, suggesting synergistic interactions between the co-adsorbates. Two-dimensional correlation spectroscopy was used to further analyze the infrared spectra. Based on this analysis, a dAMP adsorption pathway onto a pre-adsorbed phosphate hematite surface was proposed, suggesting the displacement of adsorbed phosphate by dAMP. Overall, this study provides some insights into geochemical-biological interactions on nanoscale iron oxide surfaces using vibrational spectroscopy.

Differential Surface Interactions and Surface Templating of Nucleotides (dGMP, dCMP, dAMP and dTMP) on Oxide Particle Surfaces

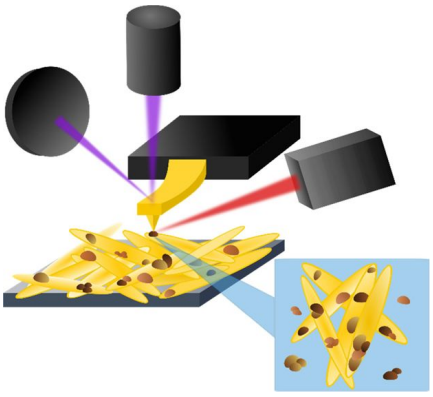
Izaac Sit, Eleanor Quirk, Eshani Hettiarachchi, Vicki H. Grassian (under review - *Langmuir*)



Abstract. The fate of biomolecules in the environment depends in part on understanding the surface chemistry occurring at the biological-geochemical (bio-geo) interface. Little is known about how environmental DNA (eDNA) or smaller component oligonucleotides and nucleotides persist in aquatic environments and the role of surface interactions. This study aims to probe surface interactions and adsorption behavior of nucleotides on oxide surfaces. We have investigated the interactions of individual nucleotides (dGMP, dCMP, dAMP, and dTMP) on TiO_2 particle surfaces as a function of pH and in the presence of complementary and noncomplementary base pairs. Using attenuated total reflectance-Fourier transform infrared spectroscopy, it is seen that there is an increase in the coverage of adsorbed nucleotides at lower pH with nucleotides interacting with the oxide surface via the phosphate group. Additionally, differential adsorption behavior is seen with purine nucleotides over their pyrimidine derivatives with purine nucleotides being preferentially adsorbed and with higher surface saturation coverage. These differences may be a result of intermolecular interactions between co-adsorbed nucleotides. When the TiO_2 surface was exposed to two component solutions of nucleotides, there was preferential adsorption of dGMP compared to dCMP and dTMP, and dAMP compared to dTMP and dCMP. Complementary nucleotide base pairs showed hydrogen-bond interactions between a strongly adsorbed nucleotide layer and weaker interacting hydrogen-bonded second layer. Noncomplementary base pairs did not form a second layer. These results highlight several important findings: (i) there is differential adsorption of nucleotides; (ii) complementary co-adsorbed nucleotides show base pairing with a second layer and the stability depends on the strength of the hydrogen bonding interactions and; (iii) the first layer coverage strongly depends on pH. Overall, the importance of surface interactions in the adsorption of nucleotides and the templating of specific interactions between nucleotides are discussed.

ATR-FTIR and AFM-IR Spectroscopic Investigation of Suwannee River Fulvic Acid and Its Interactions with α–FeOOH

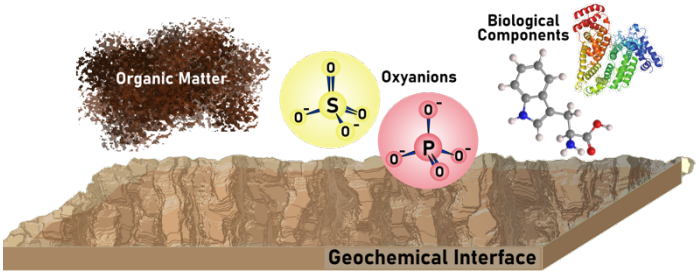
Deborah Kim and Vicki H. Grassian (published in *ACS Earth & Space Chemistry*)



Abstract. Suwannee River Fulvic Acid (SRFA) and its interaction with α–FeOOH have been investigated using two different spectroscopic probes – Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) Spectroscopy and Atomic Force Microscopy-Infrared (AFM-IR) Spectroscopy. ATR-FTIR spectroscopy of SRFA thin films yields information on functional groups present within these films prepared from solutions of three different pH values (3, 6 and 8). This technique can also be used to probe the interaction of SRFA with α–FeOOH particle surfaces and the impact that pH has on these surface interactions. AFM-IR spectroscopy offers a different perspective as it probes both film morphology and spectral signals with nanoscale spatial resolution. Here, we apply AFM-IR spectroscopy to investigate SRFA thin films and its interactions with α–FeOOH. Results from this study show that pH impacts the speciation of SRFA and its interaction with α-FeOOH. Furthermore, there are nanoscale and microscale heterogeneities in these thin films as shown in height images, point spectra and

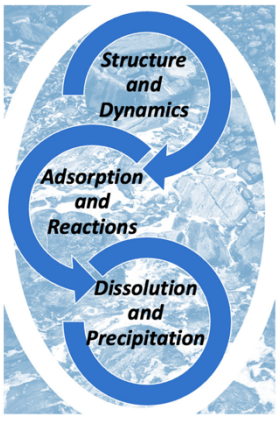
spectral maps. Overall, these measurements using two different vibrational spectroscopies provide insights into the heterogeneity of natural organic matter and its interactions with mineral surfaces.

Analysis of Micro- and Nanoscale Heterogeneities within Environmentally Relevant Thin Films Containing Biological Components, Oxyanions and Minerals Using AFM-PTIR Spectroscopy
Deborah Kim and Vicki H. Grassian (under review - *Analytical Measurements*)



Abstract. Minerals in groundwater interact with various chemical and biological species including organic matter, proteins, and prevalent oxyanions resulting in surface coatings and thin films of these different components. Surface interactions and the surface adsorption of these components on both oxide and oxyhydroxide iron surfaces have been widely investigated using a variety of spectroscopic methods. Despite these numerous studies, there still remains uncertainty with respect to interactions between these individual components, as well as heterogeneities and phase segregations within these thin films. In this study, we investigate mixtures containing Fe-containing minerals, proteins, and oxyanions to better understand surface interactions and phase segregation, using Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectroscopy and Atomic Force Microscopy PhotoThermal Infrared (AFM-PTIR) spectroscopy. The results of this study show that while ATR-FTIR spectroscopy provides important insights, AFM-PTIR spectroscopy can identify both nano- and microscale heterogeneities present within these thin films that are difficult to discern with ATR-FTIR spectroscopy due to phase segregation and mineral surface interactions. Overall, these techniques combined provide insights into multi-component environmental films that are difficult to uncover using other methodologies.

Oxide- and Silicate-Water Interfaces and Their Roles in Technology and the Environment
José Leobardo Bañuelos, Eric U. Borguet, Gordon E. Brown, Jr., Randall T. Cygan, James J. DeYoreo, Patricia M. Dove, Marie-Pierre Gaigeot, Franz M. Geiger, Julianne M. Gibbs, Vicki H. Grassian, Anastasia G. Ilgen, Young-Shin Jun, Nadine Kabengi,13 Lynn Katz, James D. Kubicki, Johannes Lützenkirchen, Christine V. Putnis, Richard C. Remsing, Kevin M. Rosso, Gernot Rother, Marialore Sulpizi, Mario Villalobos, Huichun Zhang (under review - *Chemical Reviews*)



Abstract. Interfacial reactions drive all elemental cycling on Earth and play a pivotal role in human life such as agriculture, water purification, energy production, environmental contaminant remediation, and nuclear waste repository management. Chemistry at such interfaces has been a focus of research for several decades, with the most recent comprehensive review published in 1999 (Brown et al., Chemical Reviews). Here we critically review research advances on structure, reactivity, and dynamic and coupled processes at oxide- and silicate-water interfaces in the last 20+ years and discuss the future opportunities. First, since the onset of the 21st century, strides towards a detailed understanding of interfaces submerged in aqueous solutions have been enabled by the development techniques with near-atomic measurement resolution utilizing tunable high-flux focused ultrafast laser and X-ray sources, as well as nano-fabrication approaches that enable transmission electron microscopy in a liquid cell. This leap into atomic- and nm-scale measurements uncovered scale-dependent chemical phenomena, with reaction thermodynamics, kinetics, and pathways deviating from previous observations made on the larger systems. The second key advance is new experimental evidence for what scientists

have hypothesized but could not test previously: namely that interfacial chemical reactions are frequently driven by “anomalies”, or “non-idealities” - such as defects, nanoconfinement, and unanticipated chemical structures. Third, advances in computational chemistry have allowed insight to move beyond simple schematics and gain a molecular model of these complex interfaces. These advances were facilitated by our ability to simulate with greater accuracy systems in concert with their corresponding high-resolution experimental observations. In combination with surface-sensitive measurements, we have gained knowledge of the interfacial structure and dynamics, including the underlying oxide surface and the immediately adjacent water and aqueous ions, which enable us to better define what constitutes the oxide-water interface. This critical review discusses how science is progressing from understanding the ideal oxide- and silicate-water interfaces to more realistic systems, focusing on accomplishments in the last 20 years, and identifying the remaining unknowns, outstanding challenges, and future opportunities for the community to address and/or to seek in the decades to come. We anticipate that the next 20 years will focus on understanding and predicting dynamic transient and reactive structures over greater spatial and temporal ranges as well as systems of greater structural and chemical complexity. Closer collaborations of theoretical and experimental experts across disciplines are critical to achieving this great aspiration.