Summary Report from the 2025 Interfaces for Energy and the Environment Conference (IEEC)

Conference held May 19 – 23, 2025, Richland, WA, USA
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Conference Highlights

The inaugural *Interfaces for Energy and the Environment Conference* (IEEC) took place on May 19-23, 2025, at Pacific Northwest National Laboratory (PNNL), Richland, Washington (USA). The aim of this first-of-its-kind interdisciplinary meeting was to provide a forum for participants to share the latest cutting edge experimental and computational advances in interfacial science across energy and environmental applications. The sessions below (elaborated further in the report summaries) highlighted fundamental and applied collaborative research aimed at understanding the interactions occurring at interfaces in aqueous environments, including, but not limited to, the fields of geochemistry, atmospheric chemistry, agriculture, environmental management, and catalysis. They were organized to stimulate and provide opportunities to create, renew, and deepen collaborations. The conference included activities such as oral and poster presentations, honoree mentoring session, and a team building exercise to support all career stages (detailed summaries of these activities are in the Appendices).

Over 150 participants, including scientists, engineers, postdoctoral researchers, and graduate students from national laboratories and universities worldwide, were in attendance. *Roughly 40% from PNNL, 40% universities, 10% other US national labs, 8% vendors. About 10% of participants, including keynote, invited, and contributing speakers, were foreign nationals from countries such as Mexico, Canada, Japan, Sweden, China, Germany, and France.*

Key supporters included individuals from PNNL and the Pacific Northwest Chapter of the American Vacuum Society (PNWAVS), who contributed to logistics, communications, graphic design, and vendor coordination. A comprehensive list of contributors and sponsors is in Appendix II, along with details of the discussion leaders who steered the sessions to ensure engagement and collaboration among attendees. These highlights emphasize the interdisciplinary spirit and collaborative achievements of the inaugural IEEC, leaving a strong foundation for future conferences.

Executive Summary

Interfaces for Energy and the Environment – Rationale. From radioactive waste to the longevity of forever chemicals, to carbon management, interfaces control the transport, lifetimes, and transformations of all chemical species, including critical materials, nutrients, and pollutants in the environment and the efficiency of energy systems. Studies of interfacial structure, dynamics, and reactions have reached an inflection point, driven by advances in computational and experimental methods showcased at IEEC to address fundamental mechanisms and processes that control macroscopic properties and behavior of interfaces. Molecular-level descriptions of solid–aqueous solution interfaces can explain and predict macroscopic behavior relevant to energy conversion, catalysis, and the environment.

New Advances. Major progress has been made in modeling water and solvation in aqueous solutions. Because quantum mechanical methods were unable to accurately represent delocalized electron densities in water, new ab initio and many-body approaches recast condensed-phase interactions as classical models supplemented by quantum corrections. Hybrid solvation strategies now couple explicit thermodynamic-integration simulations with continuum models using neural networks. New force fields incorporate non-linear and non-local dielectric and ionic responses and can now improve agreement with experimental differential capacitance at metal electrodes. In reactive systems, neural-network potentials (NNPs) are enabling molecular dynamics simulations of ion chemisorption on oxides, explicitly capturing the interdependence of charge transfer, solvation, and surface coordination. Continuing to push these breakthroughs to systems of greater complexity is key to understanding realistic interfaces in energy and environmental systems.

Spectroscopic and structural probes are revealing previously inaccessible interfacial details. Sum Frequency Generation (SFG) coupled with ab initio molecular dynamics (MD) resolves phonons and intermediate surface-reactive states at buried oxide–water interfaces. New measurements highlight that Electric Double Layer (EDL) relaxation follows the established Debye–Falkenhagen behavior up to ~1 M concentrations, highlighting the need for new continuum-scale models to describe high salinity solutions. Integrating phase-resolved nonlinear optics with electrochemistry enables operando tracking of molecular speciation during reactions such as the oxygen evolution reaction. Local water chemistry at interfaces can affect the subsequent interactions of ions at interfaces. Additional tools including resonant X-ray reflectivity, X-ray scattering, Raman spectroscopy, electron microscopies, and 3D atomic force microscopy (AFM) provide sub-nanometer insights into ion distributions, hydration structure, and solvent heterogeneity. These breakthroughs allow for connections between molecular phenomena and macroscopic interfacial behavior.

Key Challenges. Outstanding gaps include understanding cooperative and competitive ion effects in mixed electrolytes, defining interfacial water structure and its role in hydration, van der Waals, and correlation forces, and predicting field-dependent ion adsorption and nucleation. Long-range and many-body interactions remain difficult to capture in constant-potential MD and NNPs, and dielectric behavior in interfacial regions is anisotropic and spatially varying, making scalar dielectric constants inadequate. Activation barriers for interfacial reactions are often missing because existing solvation models cannot represent double-layer capacitance or ionic saturation. Experimentally, detecting low-abundance species, distinguishing bound versus unbound water, and quantifying ion distributions near realistic surfaces remain difficult due to sample constraints, contamination, and limited resolution. Importantly, surface defects can drive interfacial behaviors, and due to their relatively rare occurrences and structural varieties, few studies focus on them. Limited rigorous approaches for extrapolating short-term laboratory data to long-timescale environmental or geological conditions further complicates interpretation.

Future Opportunities. AI-enhanced research approaches can bring a new level of understanding to interfacial processes. Promising directions include reactive neural-network potentials enabling million-atom simulations, development of microscopic nonlocal models for screening and capacitance, and integrated solvation–electron-transfer frameworks. Improved interpretability in Machine Learning (ML) models will help uncover underlying physical mechanisms and allow for the study of large enough systems to identify highly reactive, but rare structural moieties (defects) on solid surfaces. Experimentally, higher spectral sensitivity, phase-resolved ultrafast methods, *in situ* transmission electron microscopy with ML-enabled analysis, and expanded use of neutron scattering, magnetic resonance, and surface vibrational probes will deepen insight into water and ion organization.

Finally, a major research need and opportunity exist within bridging scales and applications. Closing the gap in molecular-to-macroscale transferability is paramount. Future efforts should systematically probe kinetic controls versus thermodynamic drivers of and expand real-time characterization tools to capture evolving interfacial reactions under realistic pH, salinity, temperature, radiolytic, and nanoconfined conditions at soft and hard interfaces. Ultimately, these advances will enable the design of engineered materials with tailored interfacial properties and improve understanding of transformations in natural systems to solve critical challenges in energy, water, and environmental security.

Conference Themes

1. Theories for interface structure, dynamics, and charge transfer
   Discussion Leaders: James Kubicki, Anastasia Ilgen, Franz Geiger, and Christopher Mundy

2. Frontiers in computation and advances in analytical techniques
   Discussion Leaders: Franz Geiger, Eric Borguet, James Kubicki, and Maria Sushko

3. Abiotic and biologically-mediated nucleation, growth, and dissolution
   Discussion Leaders: Jim De Yoreo and Young-Shin Jun

4. Interfaces under complex and extreme environments: High salinity, pH, temperature, confinement, radiation and photocatalysis
   Discussion Leaders: Benjamin Legg, Emily Nienhuis, Nadine Kabengi, and Ke Yuan

5. Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies
   Discussion Leaders: Vicki Grassian, Kevin Rosso, Nadine Kabengi, and Nefeli Bompoti

6. Emerging applications and tools for energy challenges
   Discussion Leaders: Kevin Leung, Zheming Wang, Anastasia Ilgen, and Udo Becker

Theories for interface structure, dynamics, and charge transfer

James Kubicki, The University of Texas at El Paso
Anastasia Ilgen, Sandia National Laboratories
Franz Geiger, Northwestern University
Christopher J. Mundy, Pacific Northwest National Laboratory

Overview: Research presented at the “Theories for interface structure, dynamics, and charge transfer” section of the IEEC meeting focused on the development of new computational and experimental techniques to understand the evolving and reacting interfaces, defective surfaces, and the role of longer-range chemical interactions in aqueous systems.

The talks covered the behavior of bulk solutions and solutions at air and mineral interfaces. Spectroscopic methods such as non-linear optical spectroscopy and digital holographic microscopy provided unprecedented details on these topics. Advanced computational methods complemented the analytical measurements. Combinations of analytical and computational methods were used to verify modeling results and provide insights into structures, energetics and dynamics that were unobtainable from current analytical methods. The convergence in understanding of aqueous solution and interface chemistry has made tremendous progress such that consensus is strong in the field regarding the molecular-level interpretations of solution chemistry.

Figure 1 highlights the complexity even with a single crystal system of aα-quartz (101) surface having a step defect, heterogeneity, reactive flow, and nanoconfinement.[1] The sum total of the data and insights presented demonstrate that molecular-level analytical and computational techniques are increasingly able to explain and predict macroscopic behavior. This information will be valuable in designing systems to control behavior at interfaces.

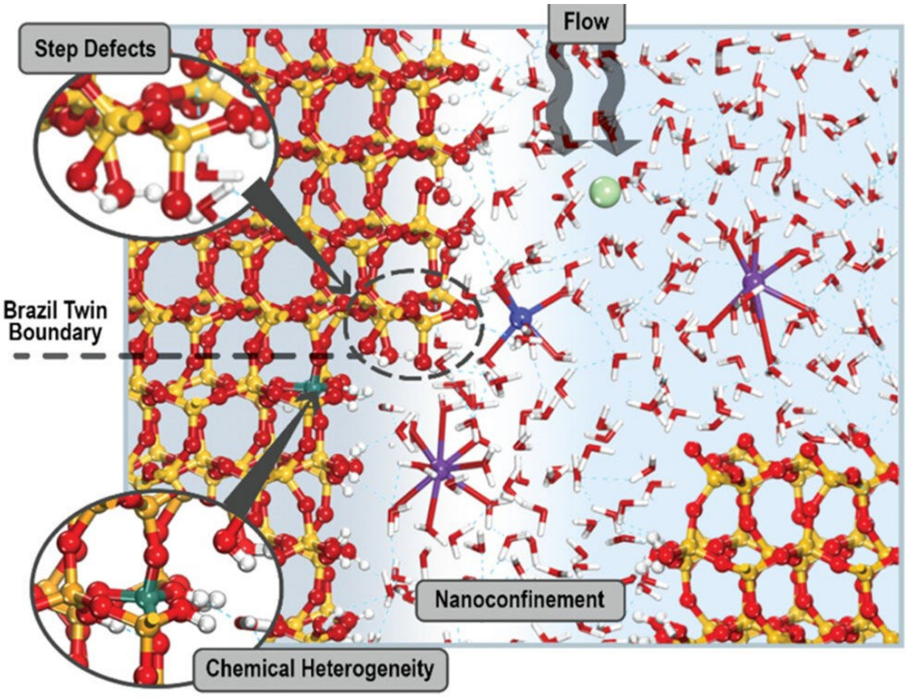

Figure 1: An α-quartz (101) surface including a step defect caused by the intersection of a Brazil twin boundary with the surface could explain the appearance of etch pits during dissolution of quartz. Furthermore, planar mineral defects such as Brazil twin boundaries could allow for compositional defects such as substitution of Fe^{3+} or Al^{3+} with H^+ replacing Si^{4+} which increases the Gibbs free energy at interfacial sites. Reproduced from ref 1. Copyright 2023 American Chemical Society.

1. State-of-the-Art Advancements

Paesani highlighted that **current Density Functional Theory (DFT) methods do** not capture bulk water behavior perfectly, necessitating **improved** ***ab initio*-based methods** to describe water's fundamental properties. This is because electron densities around water molecules should be de-localized for an appropriate representation. Many-body expansion gets around this issue and allows for realistic simulations of liquid water. In a condensed phase, many-body interactions become significant. Therefore, the quantum mechanical problem can be re-cast as a classical model of electrostatic interactions with quantum mechanical corrections. Maxwell equations were used to represent many-body electrostatics.

Gadjagboui developed a hybrid approach to predict solvation free energies by combining explicit thermodynamic integration (TI) simulations with the implicit ENVIRON continuum solvation model. A neural network was trained using the differences between implicit and explicit free energies, along with ENVIRON-based descriptors. The initial model underperformed due to limited training data, but a new dataset of ENVIRON-TI differences improved learning outcomes.

Plaisance presented VASPsol++, an extension of implicit electrolyte models that incorporated nonlinear and nonlocal treatments of the dielectric and ionic response. Previous models assumed linear screening and local cavity definitions; VASPsol++ addressed issues such as solvent leakage. Validation against the differential capacitance of Au(111) electrodes showed better agreement with the experiment than prior models.

Laage discussed the acidity at air-water interfaces, studied with DeepMD. H_3O^+ is attracted to the air-water interface, whereas OH^- is repelled. Additional complications included understanding the activity and solvation energy of H_3O^+ at the air-water interfaces, as these properties were not the same in the bulk solution at the same H_3O^+ concentration. Spectral contributions to SFG signals from surface H_3O^+ species were predicted. The rate-limiting step for H^+ diffusion is the formation of a new H-bond on the original H-bond donor to H^+, and H^+ diffusion is slower at the air-water interface compared to bulk water.

Liu used SFG spectroscopy to probe lattice vibrations at buried interfaces, resolving phonon modes associated with reactive surface sites on oxides in water. *Ab initio* molecular dynamics (AIMD) simulations identified new intermediate pathways in silica surface reactivity.

Remsing highlighted the impact of a single defect site on a surface on the local water density fluctuations and local hydrophobicity on MoS_2 surfaces (see **Figure 1** for an example). S-vacancy sites can trap electrons and make surfaces more hydrophobic, and this "trapped" state switches off catalytic activity of this surface.

Fenter discussed a common and important type of environmental system: Pb^{2+} adsorbing on calcite surfaces.[2] Heavy metals such as Pb are problematic in the environment and carbonates are found as system-dominant minerals and as surface coatings (i.e., cements) in many subsurface systems. Digital holographic microscopy (DHM) was explained as well as its utility in identifying and mapping species on surfaces. This combination is key for interfaces where adsorption and other reactions occurred at specific sites such as step defects.

Geiger presented on phase- and amplitude-resolved second harmonic generation (SHG) spectroscopy as a "photonic voltmeter" to measure interfacial potentials and calculate the number of net-aligned water molecules at solid/electrolyte interfaces. At high and intermediate ionic strengths, the measured potentials were significantly higher than predicted by the Gouy-Chapman-Stern model, indicating contributions from dipolar and quadrupolar effects.

2. Key Challenges

The key challenges identified in this session include:

(1) The need for new theories to describe long-range and many-body interactions in water and aqueous solutions.

(2) The need for new theories to predict the reactivity (e.g., acidity) at air-water interfaces of different aqueous species, particularly the activity and solvation energy of chemical species, which differ from those in bulk solutions.

(3) Understanding the impact of surface defect sites (**Figure 1**) on local solution structures, dynamics, and reactivity, which represents an exciting and challenging research area, as surface defects can significantly affect local water density fluctuations and hydrophobicity.

(4) The difficulty in predicting the impact of dissolved species on dissolution and precipitation reactions at dynamic interfaces. Experimental findings indicated an intricate coupling between chemical bond making/breaking and ion diffusion processes. Understanding the dynamics of this adsorption process, particularly in relation to mineral surfaces and their coatings, is crucial for addressing corrosion, scaling, and environmental transformations.

(5) A lack of large, diverse, and accurate training datasets as a key barrier to improving neural network-based corrections of continuum solvation models.

(6) Many DFT studies of electrocatalysts compute only thermodynamics and omit activation barriers due to the absence of tractable, accurate solvation models. Explicit solvation using DFT-based molecular dynamics (DFT-MD) is computationally expensive, and existing implicit models fail to capture essential interfacial properties such as double-layer capacitance and ionic saturation.

(7) Standard definitions of dielectric constants are invalid at interfaces, especially in nanoscale or confined systems. Interfacial water exhibits anisotropic and spatially varying dielectric behavior, making bulk dielectric models unreliable. Using fluctuation-based approaches are recommended instead.

(8) Detecting low-abundance reactive species (e.g., residual silanols) at oxide-water interfaces remains difficult, even with advanced vSFG techniques. Strong interfacial water absorption also complicates spectral resolution of oxide phonons.

(9) Doping can affect surface hydroxylation without altering bulk crystallinity. vSFG and Raman spectroscopy can detect surface changes, but XRD cannot. This limits the ability to predict reactivity and solubility in applications such as radioactive waste remediation where surface speciation is critical.

3. Knowledge Gaps and Future Opportunities

Paesani discussed accurate interatomic potentials for interfaces that can be applied to a great variety of interfaces and solution compositions.[3] The force field MB-pol[4] is an example for modeling interfaces that reproduces vibrational spectra and pair distribution functions (PDFs).

Gadjagboui's future work includes expanding the simulation and experimental dataset (>8,000 ENVIRON-TI points) and retraining machine learning models to improve solvation energy predictions.

VASPsol++ currently models ionic behavior using a mean-field approximation and lacks explicit ion-ion correlations. **Plaisance** proposed integrating classical density functional theory and hybrid solvation schemes to address these limitations.

Matyushov emphasized that dielectric constants should be redefined at interfaces using wave-vector-dependent susceptibilities or fluctuation theory. Future theoretical work will focus on developing microscopic, nonlocal models for screening, solvation, and capacitance.

Liu noted that current SFG techniques have limited sensitivity to low-coverage reactive sites (<10%) at oxide-water interfaces. Improving spectral sensitivity, spatial resolution, and theoretical interpretation of SFG line shapes is necessary to track dynamic surface reactions in aqueous environments.

Wang's results revealed a gap in conventional structural analysis: surface chemistry can change without corresponding changes in bulk structure. Future work will combine vibrational spectroscopy with atomistic simulations to investigate how dopants, radiation, and ionic strength influence interfacial chemistry in environmental and waste-processing materials.

Recent experimental and computational advances revealed new insights into interfacial phenomena but also highlighted key knowledge gaps. For example, SFG studies showed that electric double layer (EDL) relaxation at the air/water interface aligned with Debye-Falkenhagen theory up to 1 M ionic strength, yet questions remain about the distinct roles of ion diffusion and conductivity, and higher concentration limits.

Geiger highlighted that phase-resolved SFG resolved individual Stern layer water species, but distinguishing bound from unbound contributions remains difficult and the second known pK_a value of silica is not captured fully. Referencing methods that rely on assumptions about interfacial structure may have oversimplified complex, contamination-prone environments.

On the computational side, constant-potential molecular dynamics modeled solvation and charge transfer with high resolution but typically neglected long-range interactions and often treated solvation and electron dynamics independently. This decoupling may have missed key interdependencies critical to processes such as redox reactions or catalysis. Future opportunities include integrating solvation and electron transfer models and capturing the effects of nanoscale lateral heterogeneity on interfacial energy. Improving interpretability in machine learning models could also guide mechanism-driven discovery.

Frontiers in computation and advances in analytical techniques

Franz Geiger, Northwestern University
Eric Borguet, Temple University
James Kubicki, The University of Texas at El Paso
Maria Sushko, Pacific Northwest National Laboratory

Overview: The frontiers in computation and needed advances in analytical techniques are to apply these methods to increasingly complex systems and to reactive interfaces. The need to link to macroscopic behavior in real-world systems is imperative as molecular-level techniques provide insight into larger scale phenomena (**Figure 2**),[1] but the connections are limited when key aspects of environmental and energy processes are neglected.

Vibrational sum-frequency generation (vSFG) spectroscopy can supply information on H_2O orientations at interfaces and in nano-confined environments, if there is net polar ordering. However, interpretation of these spectra remains challenging. Numerous factors determine water orientations at interfaces such as ion-pairing and inner- or outer-sphere complexation. Absorptive-dispersive mixing is paramount to incorporate in line shape modeling and spectral interpretation. An example of the complexity of interpreting vSFG spectra from interfaces was provided by Li & Gaigeot who reported on pentavalent Si on the surface of silica at high pH.[5] Such an interpretation should be confirmed with other techniques such as ^{1}H-^{29}Si CP MAS NMR spectroscopy.[6]

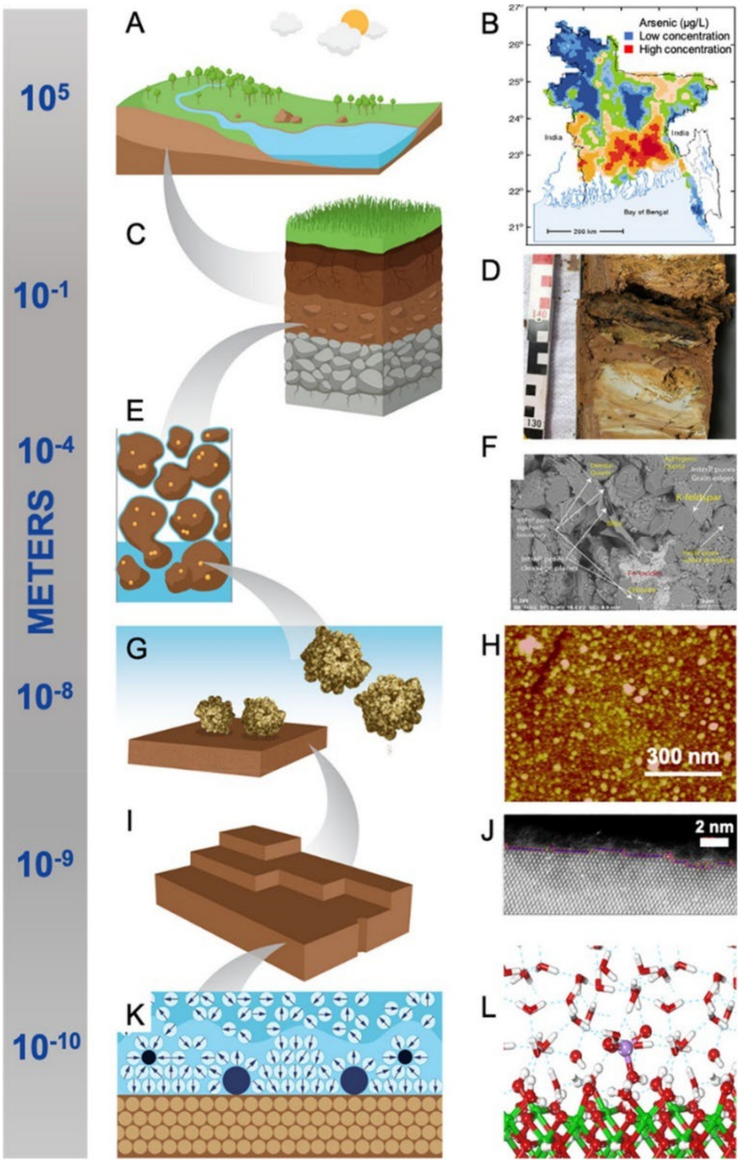

Figure 2: Scaling information from the molecular-scale (bottom) to the field scale (top) is challenging and necessary to understand environmental problems such as groundwater contamination by arsenic as depicted above. Reproduced from ref 1. Copyright 2023 American Chemical Society.

1. State-of-the-Art Advancements

Bonn showed that EDL relaxation dynamics at the air/water interface, measured via SFG, aligned well with Debye-Falkenhagen theory up to 1 M ionic strength.[7] This raised questions about the roles of diffusion and conductivity, and how vibrational modes respond to temperature changes. Further questions addressed whether electric fields exist at interfaces and how interfaces are defined. Second, Bonn talked about surface stratification determining the interfacial water structure of simple electrolyte solutions.[8] Finally, using heterodyne-detected SFG spectroscopy and the Kelvin equation, his team examined water confined between CaF_2 and 2D materials such as graphene and hBN.[9] They identified three distinct vibrational signatures for each interface, finding that confinement effects emerged only when the water layer is thinner than ~5 Å. Surprisingly, hBN showed pH-dependent charging, indicating active acid–base chemistry—unlike graphene.

Nihonyanagi used phase-resolved SFG spectroscopy and singular value decomposition to separate Stern and diffuse layer water at the silica/water interface across pH 2–12. It revealed a single pK_a of 4.8 and identified three distinct Stern layer water species—neutral, acidic, and basic—whose populations shifted with pH, offering a molecular-level view of electric double layer structure.[10]

Pezzotti reported that the amphiphilic nature (hydrophobic/hydrophilic layering) at metal–water interfaces was insensitive to whether the surface is metallic or to modest applied voltages. Instead, surface–water adhesion strength is the main control for solvation behaviors.[11] Pezzotti also demonstrated that beyond size, the shape and molecular orientation of solutes critically influenced local excess chemical potentials (which reflect the spatial variation of “solvation free energies”) at electrified interfaces, significantly affecting adsorption and catalytic activity. Using constant-potential molecular dynamics, he showed how tuning these geometric factors can optimize interfacial solvation.[12]

Rosso presented Fe(II) chemisorption on the hematite (a-Fe_2O_3) (001) surface using molecular dynamics simulations powered by a reactive neural network potential, with a focus on capturing both adsorption thermodynamics and polaron-based charge transport. The simulations reproduced key structural and kinetic features, such as water exchange rates and free energy profiles, while explicitly modeling electron and electron-hole mobility via nearest-neighbor hopping mechanisms. The study resolved distinct adsorption states—physisorbed, monodentate, and tridentate—across a solvated interface, capturing the coupled dynamics of charge, solvation, and surface coordination. This framework enables accurate modeling of Fe(II) adsorption and electron-transfer processes at complex mineral–water interfaces.[13]

Campen presented research that combined vSFG spectroscopy with electrochemistry. Simultaneously collecting vSFG spectra under *operando* condition allows for interpreting the macroscopic scale data at the molecular level. This work focused on hematite surface charge-transfer and Fe-OH speciation. Speelman performed similar studies with SHG. SHG intensities were measured as a function of applied potential to help understand the oxygen evolution reaction (OER).[14]

Kathmann discussed a relatively novel technique – electron holographic tomography – to emphasize the importance of the very strong electric fields inside atoms that are ignored in general.

2. Key Challenges

Recent experimental and computational advances have revealed new insights into interfacial phenomena but also highlighted key knowledge gaps. For example, SFG spectroscopy showed that EDL relaxation at the air/water interface aligns with Debye-Falkenhagen theory up to 1 M ionic strength, yet questions remained about the distinct roles of ion diffusion and conductivity, and higher concentration limits. Phase-resolved SFG spectroscopy resolved individual Stern layer water species, but distinguishing bound from unbound contributions remains difficult and the second known pK_a value of silica is not captured fully. Referencing methods that rely on assumptions about interfacial structure may have oversimplified complex, contamination-prone environments.

On the computational side, constant-potential molecular dynamics and neural network potentials (NNP) modeled solvation and charge transfer with high resolution but typically neglected long-range interactions and often treated solvation and electron dynamics independently. This decoupling may have missed key interdependencies critical to processes like redox reactions or catalysis. Future opportunities include integrating solvation and electron transfer models, extending frameworks such as the S.O.S. model to chemically heterogeneous surfaces, and capturing the effects of nanoscale lateral heterogeneity on interfacial energy. Improving interpretability in machine learning models could also guide mechanism-driven discovery.

The key challenge for vSFG spectroscopy and other non-linear optical methods is to probe a wider variety of minerals and complex systems. Progress was made in this area by **Geiger, Campen**, and others who are working on hematite (α-Fe_2O_3), which is representative of many Fe-oxides that are reactive environmental surfaces. A significant amount of work has focused on corundum (α-Al_2O_3)[15] as well as fused silica.[16] Ensuring that molecular modeling approaches can recapitulate observed vSFG spectra, after accounting for absorptive-dispersive mixing, is needed to benchmark modeling techniques that can be employed on a broader variety of interfaces.

Borguet investigated the possibility of determining the interfacial dielectric constant. However, this parameter is a function of distance from the surface, varying between the dielectric constant of the material and the bulk dielectric constant of solution, and may also vary in the direction parallel to the surface. Hence, it is a tensorial function of space, not a single scalar.[17]

Specific challenges include:

(1) Accounting for three-body interactions, overall water structure (hydrogen bonds angles and distances) and long-range structural changes in the description of confinement using ultrafast vibrational spectroscopy

(2) Reconciling charge regulation phenomena due to electrical double overlap in vibrational ultrafast spectroscopy

(3) Distinguishing between bound and unbound species in EDL based on polarization response

(4) Mitigating surface contamination from air organics during experiments, quickly affecting results at interfaces

(5) Extending the solid-on-solid (S.O.S.) model beyond planar surfaces to heterogeneous mineral surfaces in which the charge is delocalized

(6) Capturing the coupling between solvation dynamics and electron transfer remains a key challenge, as treating them separately can overlook critical interdependencies—particularly in modeling charge transport, where decoupled approaches may fail to represent the true complexity of the system.

(7) Interpretation and data extraction from machine learning models that often function as black boxes to physicists. An open question is whether these models can be reverse-engineered to uncover underlying physical mechanisms and guide hypothesis-driven inquiry.

(8) Capturing and correlating short- and long-range interactions in the charge-aware NNP, which primarily captures short-range interactions but effectively screens out long-range electrostatics. This simplifies the model and reduces the parameter space but also limits its ability to capture long-range coupling phenomena.

(9) Determining the critical length scale at which lateral surface features become relevant for interfacial solvation. Nanoscale surface heterogeneity significantly impacts local excess chemical potentials while microscale variations do not, thus necessitating understanding of these effects at the intermediate scale between these ranges.

(10) Referencing procedures that subtract contributions based on assumptions (e.g., silanol groups at the silica/air interface) may oversimplify interfacial complexity and overlook subtle signals present only in specific environments.

3. Knowledge Gaps and Future Opportunities

Rosso highlighted a promising method for improving molecular modeling of interfaces to be more realistic and accurate. Developing reactive interatomic potentials using neural networks showed that classical molecular modeling can be as accurate as DFT for simulating interfaces. The classical approach can be 10^6 faster than DFT calculations, so this allowed for larger (e.g., 10^6 atoms) model systems that better represented realistic pHs, ionic strengths (I), and higher molecular weight organic compounds. Umbrella sampling of a greater number of configurations also made it possible to produce accurate thermodynamics and kinetics of interfacial phenomena.

The **Campen** and **Speelman** work could be combined with the approach presented by **Rosso** to develop reliable molecular modeling interatomic potentials then expanded to other materials such as ferrihydrite (Fe_2O_3•$0.5(H_2O)$) and goethite (α-FeOOH).

The dielectric work of **Borguet** could be useful for macroscale modeling of interfaces and their effects on subsurface geochemistry (see **Figure 2**). However, complexities exist in determining the dielectric “constant” as well as translating this parameter from a single interface to complex interfacial subsurface systems.

Gonzalez examined the effects of temperature on SHG spectra at fused silica surfaces. Temperature is a key variable that has not been included in most non-linear optical studies as well as other spectroscopic methods. Because temperature increases with depth in the Earth, and many processes of interest occur at significant depth within the Earth (i.e., 1 to 5 km), temperature effects need to be more completely explored with all techniques.

Abiotic and biologically-mediated nucleation, growth, and dissolution

Jim De Yoreo, Pacific Northwest National Laboratory

Young-Shin Jun, Washington University

Overview: Nucleation, growth, and dissolution in electrolyte solutions are inherently interfacial in nature, either because they occur on existing interfaces or, in the case of nucleation, they create new interfaces either with the solution, with an underlying substrate, or both. Recent state-of-the art advances in probing interfacial systems, either at the atomic-to-molecular scale or by bridging scales have led to rapid expansion in fundamental understanding of the mechanisms by which these processes proceed with respect to both pathways and outcomes. The session discussed recent advances in experimental and modeling approaches to elucidate solid nucleation, growth, crystallization, and dissolution. Key highlights included examining the roles of interfaces—including structural, hydration, polarization, and charge distribution—on nucleation and growth, as well as facet-dependent dissolution, growth, attachment, and aggregation.

1. State-of-the-Art Advancements

Dramatic experimental advances achieved over the past decade in atomically or near-atomically resolved *in situ* experimental techniques from atomic force microscopy (AFM) to transmission electron microscopy (TEM) to X-ray imaging, combined with the increased temporal resolution of X-ray scattering due to increasingly bright light sources, more sensitive detectors, and new methods like X-ray ptychography, have enabled investigators to define the pathways and dynamics of nucleation, growth and dissolution with unprecedented detail. In particular, resonant X-ray reflectivity and 3D AFM have provided new windows into the structure of the last few nanometers of the interfacial region, which has long been a blind spot hiding the heterogeneity of solvent structure, ion distributions, and hydration forces that largely govern the events occurring at or between interfaces.

Increases in computing power have enabled molecular simulations to reach time and length scales needed to simulate adsorption of ions and molecules, nucleation both homogeneously in solutions and heterogeneously at surfaces, and phase transformations at interfaces between disparate solid phases. DFT methods can make predictions about the interactions between ions and surfaces, MD—with reactive force fields when needed—augmented by ML-derived potentials and enhanced sampling can be utilized to predict nucleation pathways and fluxes for highly soluble materials, as well as phase transformations between disparate solids. Advances in coarse graining approaches that are grounded in DFT- or ML-derived potentials of mean force have made it possible to simulate nucleation at length and time scales accessible by advanced microscopies and scattering methods.

The combination of advances in simulating and visualizing the interfacial region has enabled modifications to DLVO theory to create molecularly informed predictions about colloidal interactions based on more accurate descriptions of van der Waals (vdW) interactions, nanoscale hydrodynamic forces, and long-range electrostatic forces, including vdW and electrostatic torques that play a key role in systems of anisotropic mineral particles. Taken together, these advances truly place the field on the verge of a predictive capability for the processes of nucleation, growth and dissolution, which can predict reaction mechanisms and kinetics more accurately, and help us to design nanomaterials properties in nature and engineering applications (**Figure 3**).[18]

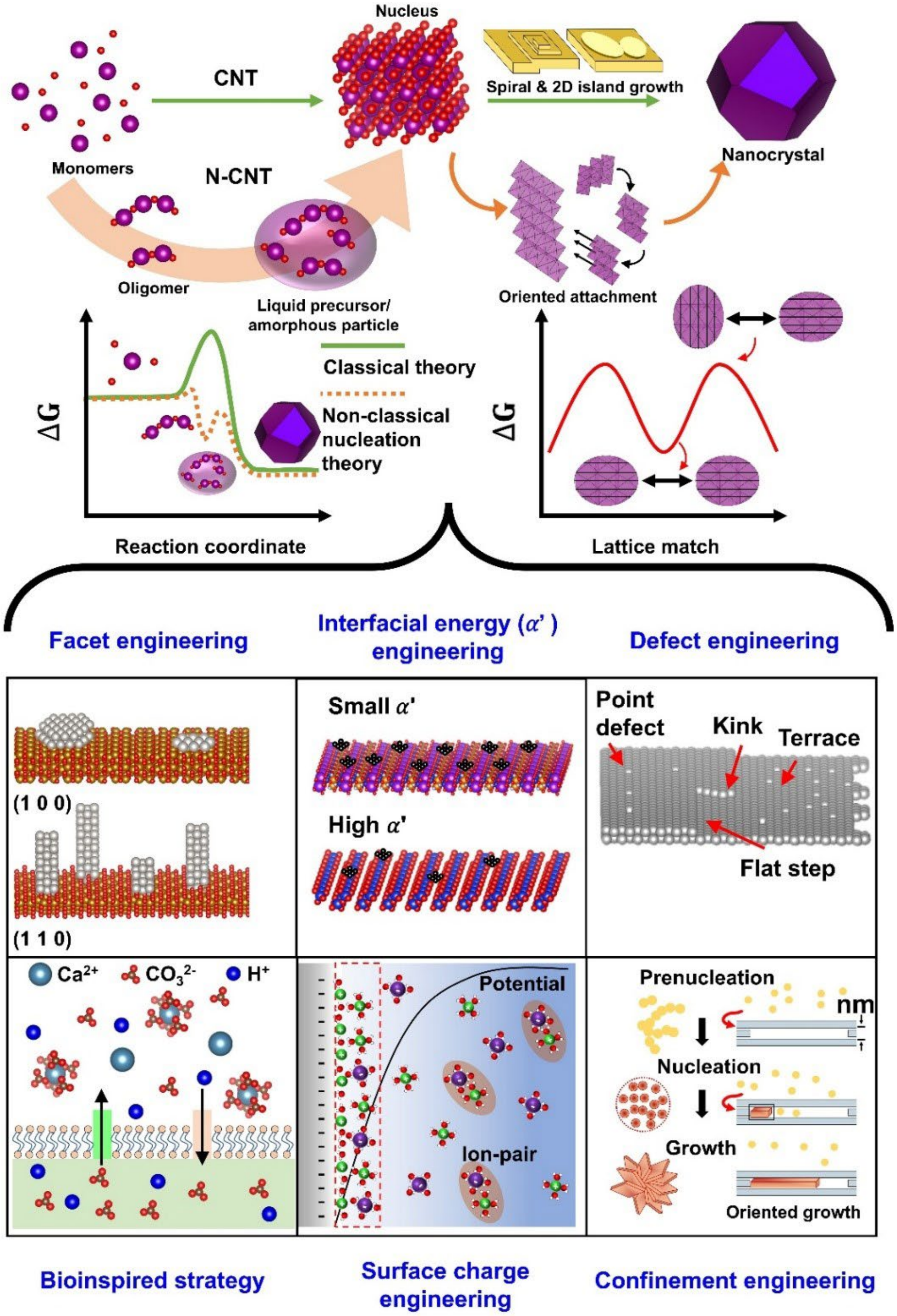

Figure 3: Classical and nonclassical nucleation and growth mechanisms and key controlling factors in engineering nanoparticles and understanding their behavior. Theoretical and experimental approaches can yield a comprehensive model connecting the nucleation and the growth behaviors of nanoparticles. Such model development can predict the behavior and formation of nanoparticles more accurately enabling us to design and predict their properties in engineering fields and nature. Reproduced from ref 18**.** Copyright 2022 Annual Reviews.

Jun discussed solubility-controlled nucleation and lattice mismatch-controlled growth for critical element recovery from low-grade ores. In solutions with cobalt and magnesium ions, cobalt carbonate forms a core first, followed by a magnesium carbonate shell. Lattice differences in such heteroepitaxial nucleation and growth create nanochannels in the shell, aiding sulfide transport. Cobalt carbonate then transforms into cobalt sulfide, while magnesium carbonate remains intact. Selective oxidation with hydrogen peroxide recovers cobalt, leaving magnesium carbonate unaffected. Thus, controlling nucleation and dissolution enhances critical element recovery.

Shen performed MD simulations of amorphous carbonate nucleation on silicate surfaces. The silicate surfaces drew water molecules from the carbonate nuclei, forming a partial hydration layer that disrupted the amorphous carbonate structures. Consequently, the calculated interfacial energies favored homogeneous nucleation of amorphous carbonates over heterogeneous nucleation. This study highlighted how MD simulations provide atomic-level insights into a nonclassical growth mechanism.

Sushko introduced a hybrid approach combining first-principles plane-wave DFT with classical DFT (cDFT). Simulations of calcite (104)/solution interfaces revealed key polarization interactions that structure ions and water. This method can predict electric double layer (EDL) structures at mineral surfaces, aiding accurate modeling of sorption, nucleation, dissolution, and growth in complex solutions.

Taylor studied competitive growth and dissolution processes on hematite crystallites with Fe(II) and/or oxalic acid. The study showed that Fe(II) oxidative adsorption occurs on (001) and (012) hematite surfaces without oxalate, but with oxalate, selective dissolution of the (001) surface prevails. The findings highlight the anisotropic reactivity of iron oxide surfaces, crucial for assessing and predicting their effectiveness as environmental catalysts.

X. Zhang examined oriented attachment (OA) mechanisms in metal oxide systems and their relation to interfacial structure. The research revealed: (i) aggregation-driven crystallization of hematite is orientation-dependent, not based on exposed facets; (ii) monodisperse gibbsite nanoplates (~100 nm) form hexagonal columnar mesocrystals (~100 μm) upon water evaporation; and (iii) anisotropic forces between rutile TiO_2 (001) nanocrystals depend on azimuthal alignment and hydration.

Bae investigated the formation of branched cubic Pt mesocrystals through OA in electrolyte solutions. Attachment starts on the {100} facets, forming a cubic core, then shifts to the {111} facets, leading to branched rod growth. The study shows that anisotropic electrostatic interactions and resulting torques govern OA directionality, offering valuable guidance for designing complex nanostructures with tailored properties.

Nakouzi presented three case studies: (i) Extreme salt concentrations enhance ion correlations at boehmite nanoparticle surfaces, leading to strong repulsive forces and decreased aggregation. (ii) Ligand-coated nanoparticles' incorporation in growing calcite crystals depends on their penetration into interfacial hydration layers and binding energy upon adsorption. (iii) Oxidizing a plastic surface makes polymer-water interfaces hydrophilic, increasing the propensity for ice nucleation.

M. Zhang used 3D AFM to determine solution structure and hydration forces, dynamic force spectroscopy (DFS) to measure binding energy, and confocal fluorescence microscopy to quantify nanoparticle incorporation. Compared to a bare PEG probe, hydroxyl groups lower hydration forces, reducing kinetic barriers, while carboxyl groups increase binding energy. Monte Carlo simulations show that hydration forces affect collision frequency, and binding energy determines particle surface lifetime.

Zorman introduced a self-consistent multiscale framework for simulating NaCl and $CaCO_3$ nucleation at physiological concentrations. The framework uses both continuum and lattice-based Monte Carlo methods, reconstituting into all-atom Molecular Dynamics simulations. The lattice model precisely handles long-range interactions, accurately predicting speciation distributions and nucleation rates for NaCl and $CaCO_3$.

2. Key Challenges

Amongst the technological challenges that inhibit fundamental advances in the interfacial science of nucleation, growth, and dissolution are our continuing limited ability to quantify the distribution of ions in the interfacial region. Resonance X-ray reflectivity has been an important method in this regard, but the range of ions that can be probed is limited and large atomically flat single crystal surfaces are required. 3D AFM has proved a promising method, but differentiating between contributions from solvent *vs.* hydrated ions requires molecular simulations, which must account for the effect of the tip and the real structure of surfaces, including surface protonation states.

For numerous systems, particularly those involving organic and macromolecular films, the nature of the interfacial region between film and mineral substrate remains a mystery. An effort to apply methods like dynamic nuclear polarization nuclear magnetic resonance (NMR), neutron scattering, grazing incidence X-ray scattering, and surface vibrational spectroscopy (including surface-enhanced Raman spectroscopy) are needed to begin establishing an accurate picture of this region.

The introduction of complexity extends to the problem particle-based growth processes. Colloidal science is well established for systems of isotropic spheres and rods with simple interactions. However, mineral systems inherently involve particles that have anisotropic shapes and properties that include surface charge, dielectric constant, surface defects, chemical heterogeneity, roughness, and hydration structure. Consequently, the interactions—both the attractive and repulsive forces—are anisotropic, leading to deviations from predictions for traditional colloidal systems that are still poorly understood.

In addition, the nucleation, growth, crystallization, and dissolution of solids in nanoconfined interfaces are not well understood. Nanoconfinement alters the structure, dynamics, and thermodynamics of water, changing the solvation free energies of ions and clusters and affecting ion-pair formation. This impacts solid nucleation, growth, and dissolution in nanopores. The dominance of solubility or interface-controlled nucleation in nanoconfinement varies across systems and remains unclear.

3. Knowledge Gaps and Future Opportunities

Defining interfacial ion distributions remains a significant challenge. Furthermore, classical nucleation theory (CNT) includes reaction pathways, but many systems follow pathways not captured by CNT. Therefore, more general theoretical and quantitative frameworks for nucleation with multiple pathways (non-CNT) are needed. These processes can be simulated using reactive force fields or DFT to define reaction parameters, which can then be incorporated into coarse-grained models for larger systems.

Several knowledge gaps define significant research opportunities for the future including:

(1) The impact of competing and cooperating ion effects in mixed electrolyte solutions and solutions of electrolytes and organic ligands;

(2) The effects of electric fields on ion adsorption and nucleation at surfaces;

(3) The source of interfacially-driven nucleation near mineral surfaces;

(4) The structure of water and ion distributions near interfaces and their impact on hydration, vdW, and ion correlation forces;

(5) The impacts of nanoconfinement on the nucleation, growth, crystallization, and dissolution of solids;

(5) The basis of facet selectivity and attachment dynamics during OA, particularly for anisotropic and rough particles.

Filling these gaps promises achievement of broadly predictive capabilities for nucleation, growth, and dissolution, whether through classical or non-classical pathways.

Interfaces under complex and extreme environments: High salinity, pH, temperature, confinement, radiation, and photocatalysis

Benjamin Legg, Pacific Northwest National Laboratory
Emily Nienhuis, Pacific Northwest National Laboratory
Nadine Kabengi, Georgia State University
Ke Yuan, Oak Ridge National Laboratory

Overview:
This session explored the behavior of interfaces under complex and extreme environments, which span from high salinity, pH, temperature, confinement, radiation, to photocatalytic conditions. Talks collectively emphasized how interfacial phenomena, coupled with local chemical heterogeneity and confinement, control molecular-scale solvent and ion dynamics, redox transformations, and material stability under extreme conditions.

1. State-of-the-Art Advancements

Presentations in this session highlighted cutting-edge advancements that bridge fundamental understanding of interfacial processes with applications in separations, catalysis, and nuclear waste management. A series of talks by Chong Liu, Haoyuan Shi, and Tuan Ho examined how nanoscale confinement influences solution structure, ion transport, and viscosity. Particularly, studies of functionalized MoS_2 channels demonstrated the ability to provide ion-selective transport (with exciting potentials for separations applications), wherein understanding the origins of selectivity and cooperative behavior between ions.

Liu showed non-linear relationships between ion mobility and hydration enthalpy, emphasizing the need for optimized solvation and surface affinity (**Figure 4**).[19]

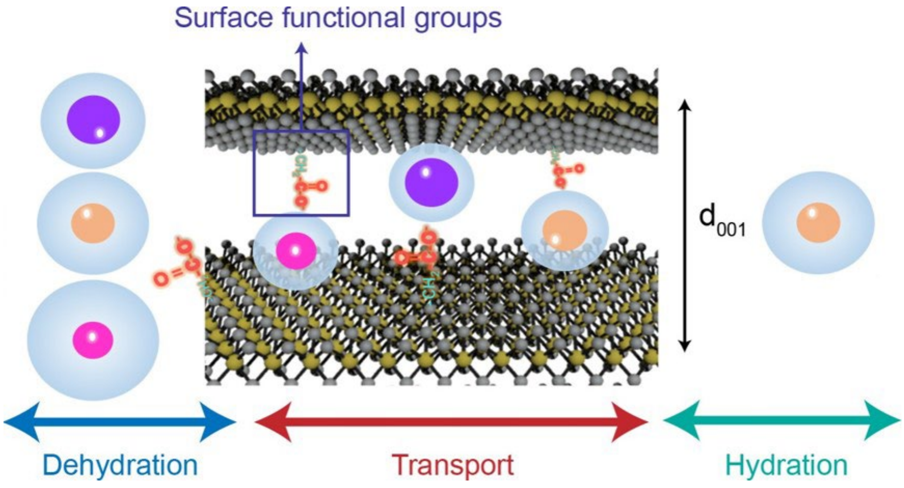

Figure 4: Schematic diagram for the transport of REE ions in the MoS_2-COOH 2D channels. Image from ref 19, open access journal.

Molecular simulations from **Ho**'s talk further illuminated cooperative ion transport, demonstrating that NaCl pairs transport distinctly from lone Na^+ or Cl^- ions in nanopores. This work also showed that in some cases (i.e., gibbsite), pair transport is highly favored, while in others (kaolinite), it determines on the types of ions.

Shi's simulations showed how such physics are not only relevant to ion-transport, but also to fluid flow. Using Green-Kubo simulations, Haoyuan demonstrated how changes in dynamics and structure near surfaces relate to bulk transport properties such as slip-plan location and slip length.

Complementary experimental work extended these interfacial insights to radiation- and redox-driven environments.

Ilgen presented water adsorption in oxide and silicate nanopores in vapor-phase systems. The results emphasized how factors such as surface hydrophilicity and pore geometry can change adsorption modes, including site-specific adsorption site energy. This work highlights that classical thermodynamics struggle to predict how nanoconfinement will impact the energetics of surface complexation reactions, including simple hydrogen-bonding between water molecules and surfaces. .

Felsted and **Nienhuis** presented new methods to probe interfacial processes under high pH, ionic strength, and radiation, where laser-induced fields can trigger nucleation and chemical transformations in concentrated electrolytes. Advanced 2D IR spectroscopy provided new insights into ion proximities and coupling among functional groups in complex aqueous environments.

Extending the theme to radionuclide chemistry, **Becker** showed the redox behavior of uranium clusters through a combination of electrochemistry and quantum mechanical simulations. Cyclic voltammetry showed multiple reversible redox transitions of U_{60} nanoclusters. By integrating oxidation state-dependent binding energy calculations into Pourbaix diagrams, more accurate redox peak assignments, and deeper insights into the reactivities of U clusters were uncovered.

Carbone et al. elucidated the reduction of U(VI) to U(IV) via a previously unconfirmed U(V) intermediate using electron energy loss spectroscopy (EELS) and first-principles calculations. Their work bridged the characterization of U valence states with macroscale implications for their environmental mobilities.

Saslow et al. introduced hybrid ion-exchange resins for multi-contaminant removal (Tc, Cr, U, I) at the Hanford Site. Dual-resin systems like ResinTech's SIR-700-HP and SIR-110-MP-Ce show promising results for treating uranium, technetium, chromium, and iodine contaminants within the shared plumes.

Hong et al. and Kerisit et al. presented advances in Cs sequestration and glass corrosion modeling, demonstrating how molecular-level processes govern long-term environmental stability of nuclear waste forms.

Kerisit et al. presented a validated glass corrosion model that integrates dissolution kinetics, ion exchange, and pseudo-equilibrium to predict the release of radionuclide from borosilicate glass at long time scales (over thousands of years).

High ionic strength and elevated temperature conditions were studied using phase-resolved second harmonic generation by **Gonzalez and Geiger**, as discussed above in "Frontiers in computation and advances in analytical techniques."

2. Key Challenges

Despite these advancements, several grand challenges persist.

(1) Predicting ion-specific transport and separations in confined and extreme environments requires integrating experimental and theoretical approaches that capture coupling between solvation, confinement, and interfacial chemistry.

(2) Quantifying ion dynamics, local solvation structures, and cooperative interactions in complex systems that may not be fully equilibrated or are intrinsically non-equilibrium states remains difficult.

In the nuclear waste context, directly identifying metastable intermediates such as U(V) continues to challenge both spectroscopic and computational methods, as complex mixed-valence states demand extensive databases and advanced modeling.

(3) Understanding how confinement, crystal morphology, and pore-scale heterogeneity control radionuclide mobility, Cs leachability, and long-term corrosion behavior in glass waste forms remains incomplete.

(4) Extrapolating from short-term laboratory studies to geological time scales.

3. Knowledge Gaps and Future Opportunities

Addressing these challenges calls for coordinated advances in experiment, simulation, and modeling. **Felsted** highlighted new opportunities in ultrafast pump-probe systems, which have the potential to understand direct couplings between molecular states, local structures, and dissipation of energy. Current demonstrations focus on exploiting these in high-concentration environments and reveal ion-solvation. Potentials to extrapolate these techniques towards interfacial systems (i.e., where solvation is coupled to transport) are an exciting potential future application. The novel experimental approaches, such as Dynamic Vapor Sorption Analyzer provide opportunities to link structure to thermodynamics. And simulations are still proving highly important; helping reveal complicated couplings that would be difficult to disentangle from experiment alone.

In parallel, opportunities exist to extend molecular-scale models to field-scale predictions, such as bridging uranium redox chemistry to contaminant transport or connecting nanoscale ion selectivity to membrane performance. Future directions include real-time tracking of metastable species to elucidate redox pathways, leveraging AI and machine learning to develop predictive corrosion and separation models, and conducting multiscale simulations to understand how waste forms and sorbents interact with complex mixed contaminant systems. Collectively, these approaches will enable a more predictive framework linking interfacial dynamics under extreme conditions to environmental remediation, materials stability, and energy technologies.

Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies

Vicki Grassian, University of California, San Diego
Kevin Rosso, Pacific Northwest National Laboratory
Nefeli Bompoti, University of Massachusetts, Dartmouth
Nadine Kabengi, Georgia State University, Atlanta

Overview

The session showcased cutting-edge approaches to understanding interfacial phenomena across molecular to macroscopic scales and in diverse applications ranging from environmental remediation to energy and water technologies to technological approaches to climate change.

1. State-of-the-Art Advancements

Talks in this session focused on state-of-the-art approaches to investigating and understanding interfacial phenomena at the molecular scale and then using this information to further understand the global impacts of interfaces in energy and the environment.

Grassian emphasized how interfacial chemistry of oxide and silicate surface chemistry at solid/air and solid/water interfaces influences global processes including atmospheric processes in the troposphere, solar radiation management in the stratosphere, and adsorbed biomolecule structure and stability in aqueous systems. She underscored the need for cross-disciplinary approaches and for probing surface reactivity under realistic, complex environmental conditions.

Kubicki highlighted the role of molecular computation in resolving problems not easily accessed experimentally. His DFT studies on quartz dissolution revealed how chloride ions facilitate proton interactions at surfaces and how peroxide bond formation in quartz grain boundaries favors H_2 release. He emphasized the value of integrating theory and experiment for mechanistic insights.

Pearce presented work from the IDREAM Energy Frontier Research Center using advanced AFM and RadAFM tools to study aluminum (oxy)hydroxide dissolution in Hanford tank waste. Findings revealed unexpected mechanisms, such as dimeric aluminate detachment and inhibition by adsorbed carboxylates or chromium, with implications for radionuclide mobility.

Kelly investigated pore-scale crystallization dynamics through simulations and microfluidic experiments. Studies showed how pore geometry and flow regime influence CO_2-water reactions in geologic carbon storage and how non-equilibrium flow conditions alter crystallization pathways, diverging from classical thermodynamic predictions and the implications this has for developing methods for carbon storage.

Additional contributions highlighted novel spectroscopic and computational approaches for studying mineral-water interfaces, namely the pyrite (001)-water interface under low oxygen partial pressures, conditions relevant to suboxic environments. The hydration of metal carbonates, as well as the structural properties of micro- and nanocrystalline carbonates, provided insights into the uptake capacity and stability of these long-term carbon dioxide storage materials. Other talks presented engineered Cu and graphene surfaces with tailored wettability and porosity to improve thermal and fluid transport efficiency in desalination processes, as well as spectral induced polarization as a noninvasive tool to monitor remediation processes.

2. Key Challenges

Interfacial science plays a pivotal role in addressing critical energy and environmental challenges, yet several grand challenges continue to impede the translation of fundamental discoveries into practical, scalable solutions. Discussion leaders collectively noted several grand challenges:

(1) Bridging both length and time scales (from molecular to macroscopic, and from picoseconds to decades) remains a central challenge,

(2) Dynamic, non-equilibrium interfacial processes are still difficult to observe and model with high fidelity, thus limiting predictive capacity,

(3) Complex multi-phase and heterogeneous environments, including radiolytic fields and adsorbate effects, introduce uncertainties that current models often oversimplify,

(4) Transferability of thermodynamic and kinetic parameters across conditions and systems hampers accurate environmental and reactive transport predictions

3. Knowledge Gaps and Future Opportunities

One of the major knowledge gaps outlined in this session is the molecular-to-macroscale transferability (**Figure 5**) -closing this gap is key. Despite cutting-edge spectroscopic and computational approaches, a significant gap remains in connecting molecular-scale interfacial behavior to macroscale applications. In addition, most techniques focus on equilibrium or near-equilibrium states. Yet, in real-world applications, such as desalination and reactive transport, interfacial processes are often occurring far from equilibrium and undergo constant fluctuations as a function of environmental conditions such as pH and redox.

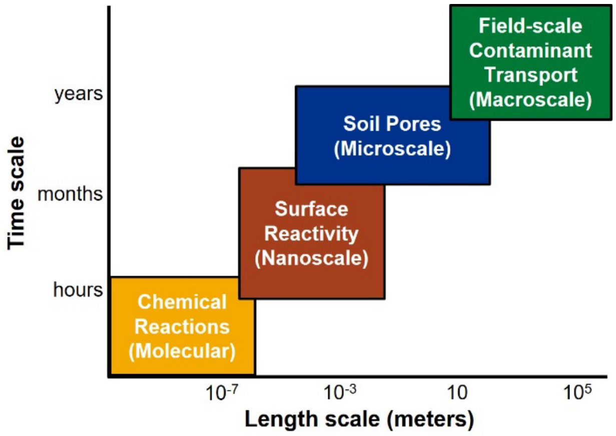

Figure 5: Interfaces across spatiotemporal scales, from molecular-level chemical reactions and surface reactivity to meso-scale features such as soil pore structures and mineral-fluid boundaries. Contaminant transport studies exemplify the significance of interfacial science in addressing societal problems.

Several future opportunities were highlighted, including: (i) Expanding real-time characterization tools (AFM, TEM, synchrotron, microfluidics and beyond) to capture evolving interfacial reactions under realistic and radiolytic conditions, (ii) Integrating experimental and computational advances—including machine-learning-accelerated molecular dynamics—to better connect quantum-level accuracy with larger scale, complex environments, (iii) Linking geochemistry and environmental geophysics to improve modeling and monitoring of contaminant mobility and remediation, (iv) Systematic probing of kinetic vs thermodynamic drivers of mineral formation using microfluidic analogues, and (v) Designing engineered materials (graphene, oxides, carbonates) with tailored interfacial properties to address energy, water, and environmental challenges.

Emerging applications and tools for energy challenges

Anastasia Ilgen, Sandia National laboratories
Udo Becker, University of Michigan
Kevin Leung, Sandia National Laboratories
Zheming Wang, Pacific Northwest National Laboratory

1. State-of-the-Art Advancements

Research presented at the "Emerging applications and tools for energy challenges" session at the IEEC meeting focused on understanding applications related to carbon dioxide (CO_2) mineralization, machine-learning-based modeling of surface contaminant interactions at oxide interfaces, novel spectroscopic analysis, ion-solvent-surfactant interactions, ion diffusion across interfaces, and ion separations.

A significant portion of this session dealt with reactions at air- and mineral-water interfaces that lead to CO_2 capture and conversion. New approaches were presented on molecular-scale interactions and applications of mineral surfaces and other materials.

Boamah-Agyemang et al. presented research using vibrational sum frequency spectroscopy (vSFG) to understand the hydroxylation and carbonation of forsterite surfaces, revealing how humidity levels influence the presence of hydroxyl groups and CO_2 interaction and mineralization, which is crucial for enhancing direct air capture technologies.

Song et al. gave theoretical insights into the dissolution of magnesium from hydrated forsterite, identifying the terrace-step $(04\bar{1})$ surface as a key site for magnesium dissolution through *ab initio* calculations.

Tyrode's study on fatty amine monolayers at the air-water interface elucidated their acid-base behavior and interactions with gas-phase CO_2, utilizing vSFG to uncover carbon capture mechanisms. This may be a viable way to temporarily capture CO_2 that can then be retrieved for terminal storage.

Perrine's work emphasized mineral carbonation that proceeds via the precipitation (and oxidation) of iron-oxide minerals as films at the air-water interface, employing *in situ* polarized modulated infrared reflection absorption spectroscopy to explore how ions and acidity affect CO_2 adsorption and mineral film formation. Transitioning from carbon capture to the role of light on interfaces, **Shultz et al.** explored the potential of anatase titania photocatalysts for pollution reduction and CO_2 conversion, demonstrating that ultra-nanoscale (< 2 nm) particles enhance photocatalytic efficiency through systematic doping (e.g., using Pt or Fe), which influences charge-carrier dynamics and product formation pathways.

Anwar and **Tagliabue** introduced a unified framework for hydrovoltaic devices that convert ambient heat into electricity (via evaporation), showcasing significant power output enhancements through innovative material design achieved with nano-pillar architecture.

For other applications, machine learning is starting to emerge as a technique to gain insights into interfacial chemical reactions. In the opening talk of the session, **Mason** incorporated stochastic and machine-learning-driven approaches to explore non-intuitive interfacial structures and property-descriptor relationships for contaminant (oxyanions, heavy metals, and organic species) binding energetics on model solid minerals such as hematite (α-Fe_2O_3) and alumina (α-Al_2O_3), extending the understanding to emerging materials like MXenes and those used in nano-enabled agriculture.

Young reported using an end-to-end automatic analysis pipeline utilizing four specialized convolutional neural networks (CNNs) that process raw spectra, realizing de-noising, background removal, peak detection, and peak intensity and FWMH retrieval. For de-noising, hierarchical UNET architecture outputs smoothed spectra with a mean squared error below 2.26×10^{-4} %, while the use of a pyramidal UNET architecture for baseline removal, achieving a mean squared error below 6.38×10^{-4} %. For peak detection, a deep-cascading UNET-hybrid architecture coupled with an in-house loss function demonstrated 94.1% accuracy compared to 81.7% with traditional cross-entropy and mean square error loss approaches. The automated pipeline significantly improved the efficiency and objectiveness of spectroscopy data processing by minimizing the human intervention, eventually contributing to high throughput data analysis and large-scale spectroscopy dataset construction.

The advances in the experimental domain include complementary technical approaches of the use of surface X-ray/Neutron scattering and spectroscopy with vibrational sum frequency generation spectroscopy which is a powerful approach to improve understanding of interfacial ion–ion, ion–surfactant, and ion–solvent interactions.

As ion transfer across phase boundaries is a key process in separation science, particularly for rare earth and other critical element separations either from the bulk solution or among these ions, gaining knowledge about the molecular structure and transport kinetics in these separation processes will have a pronounced impact in both the underlying fundamental science and the process economy. Using a combination of X-ray fluorescence near total reflection (XFNTR) and vibrational sum frequency generation (VSFG) spectroscopy, both are interface-selective techniques, detailed pictures of pseudo halide adsorption at positively charged interface, trivalent ion adsorption at soft charged interfaces, and ion-specific monolayer to bilayer transition as well as how these processes are affected by ion concentration and electrolyte concentration were demonstrated at the molecular scale.

Several talks in the Tuesday afternoon “Emerging applications and tools for energy challenges” sessions offer good examples to bridge scales between the molecular and macroscopic details. While both XFNTR and VSFG provide the spatial and molecular structural and orientational information of the sub-nm thickness interfacial molecules, the work presented by **Chen** and **Ricchiuti** connects interfacial phenomena with bulk properties.

Chen proposed a two-layer interfacial model with an organic-rich layer that facilitates cation desolvation and an inorganic amorphous layer that allows for Mg^{2+} diffusion across the interface.

Ricchiuti’s work showed that ion separation at interfaces arises from preferential accumulation or distribution relative to the bulk solution and these interfacial separation processes are influenced by electrostatic forces, ion-solvent interactions, and external fields. Differences in Co^{2+} and Ni^{2+} susceptibilities allow magnetic control of ion accumulation, while combined magnetic and electric fields enhance charge transfer for selective, morphology-controlled deposition. In another example, the application of magnetic fields enriched 5 mol% of Dy^{3+} ions in 20 seconds, versus less than 1 mol% for La^{3+} ion, forming the basis of magnetically driven separation systems.

2. Key Challenges

Despite these advancements, several challenges remain in the field. For CO_2 applications, the dissolution mechanisms of forsterite and the role of guest inclusions are still debated, as highlighted by **Song et al**. This is one aspect of evaluating whether CO_2 storage is a safe and long-term solution. Additionally, while the photocatalytic efficiency of materials like anatase titania has improved, the variability in results across different studies indicates a need for more standardized catalyst design and testing approaches. The complexities of mineral carbonation processes, as discussed by **Perrine** and **Boamah**, also underscore the need for a deeper understanding of the factors influencing mineral film growth, local structure of reactive surfaces, and CO_2 adsorption/incorporation into mineral phases.

Other general, major technological challenges inhibiting fundamental advances in interfacial science are

(1) Shortage of data (information), particularly those of high quality, to be used in implementing computational and ML-/AI-based technologies and the relevant databases;

(2) More powerful computations, encompassing larger systems and longer time-scales to represent complex interfacial systems;

(3) High throughput experimental analysis. Progress in addressing these challenges will allow better understanding of more complex and "buried" systems.

Topics not covered in the talks but discussed in the session Introduction are i) Interfacial studies of "dirty" (i.e., thin surface film-covered metal) electrode surfaces and ii) expanding molecular-level interfacial studies to broader, more applied fields as currently available mostly for pristine, model chemical systems. Thin, passivating film-covered metal surfaces are foundational to the study of structural material corrosion and to high energy density battery (e.g., lithium/sodium/magnesium metal) anode surfaces. The surface films act as dielectric barriers and/or solid electrolytes in which most of the applied potential is manifested, causing qualitative changes in the "electric double layer" normally found within the liquid electrolytes. The resulting, large spatial charge-separation length-scales make the fitting to machine-learning interatomic potentials particularly challenging. Current basic science studies of liquid-metal interfaces have mostly focused on pristine metal electrodes, which leads to a barrier in understanding interfaces in many realistic systems. Overcoming these challenges will allow breakthroughs in many economically important science and engineering areas from Energy and Climate Resilience, Global Water Security, Catalysis, and/or Critical Materials, Environmental Remediation, Renewable Energy, and Separations.

3. Knowledge Gaps and Future Opportunities

There are notable knowledge gaps that present future research opportunities. For instance, while **Zarzycki** addressed isotopic fractionation at mineral/electrolyte interfaces, the lack of experimental methods to study these processes limits our understanding of isotopic behavior during mineral growth, including during the carbonation of abundant minerals. Overall, these studies pave the way to further explore the mechanisms underlying mineral interactions and material behaviors relevant to CO_2 capture, as well as conversion into either carbonate minerals or other compounds (**Figure 6**),[20] with the potential to advance carbon management technologies and sustainable energy solutions. While new and exciting experimental and computational approaches were presented, one major key challenge is to scale these avenues up to a macroscopic level to judge if CO_2 storage is a safe, cost-efficient, and viable way to address CO_2 reduction.

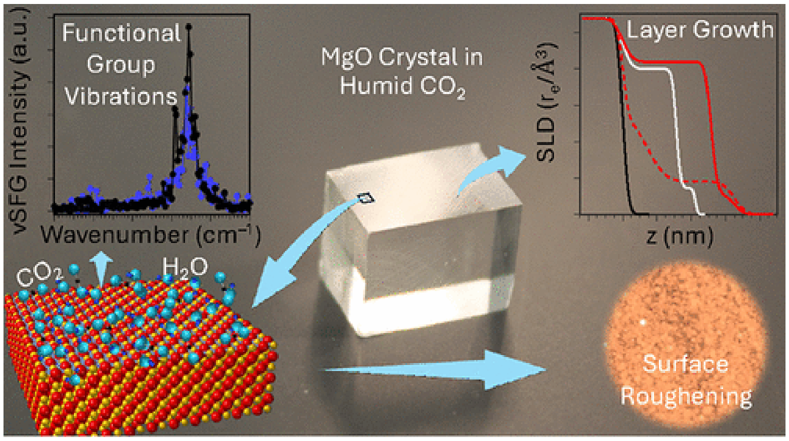

Figure 6: MgO reacted with atmospheric CO_2 under humid condition was examined by X-ray scattering, microscopy, and vibrational spectroscopy. Results showed that the carbonate phase formed as barringtonite ($MgCO_3 \cdot 2H_2O$) and nesquehonite ($MgCO_3 \cdot 2H_2O$). Reproduced from ref 20. Copyright 2025 American Chemical Society.

Other general gaps and opportunities include: i) interfacial chemistry in multivalent-ion system, particularly in far away from diluted solutions; ii) mechanisms and major parameters affecting external field-driven separation chemistry; iii) hydration/solvation in mixed polar-nonpolar systems, particularly relevant to critical element extraction and separation; iv) the calculation of solvation free energies in confinement at finite salt concentrations, especially for multivalent systems.

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- Shuttha Shutthanandan (Web Designer, PNNL)
- Theva Thevuthasan (Vice Treasurer, PNNL)
- Heather Roney (Local Arrangements, PNNL)
- Melissa Perdue (Communications, PNNL)
- Melanie Hess-Robinson (Graphic Design, PNNL)
- Douglas Jones (Treasurer, PNWAVS)
- Joe Gray (Vendor Representative, PNWAVS)

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APPENDIX I: Conference activities

Poster awards

A student poster competition was organized to recognize talented postdoctoral and graduate students and their outstanding contributions to the field. Various disciplines were represented from critical materials extraction to biomineralization. Participant posters were judged for their presentation and research quality. First, second, and third place was awarded to the highest scoring postdoctoral participants as well as graduate student participants. The first-place postdoctoral awardee was Benjamin Jackson (PNNL) for his work on “Interactions of polar and non-polar groups of alcohols in zeolite pores.” The first-place graduate student awardee was Jack Grimm (University of Washington, PNNL) for his work on “Determining whether de-/re-mineralization or intergranular diffusion cause compositional gradients in human dental enamel.” Honorable mentions were also given to 2-3 high-ranking posters, providing further recognition of talented postdoctoral and graduate students.

Honoree sessions

Several senior leaders in the field of interfacial science were recognized with the “Interfacial Chemistry Excellence Award” during the dinner banquet on Wednesday, May 21st, 2025.

- Dr. Randall Cygan, Sandia National Laboratories - Senior Scientist (retired), Texas A&M University - Adjunct Professor
- Prof. Gordon Brown, Stanford University - Dorrell William Kirby Emeritus Professor of Geology in the School of Earth Sciences
- Prof. Alexandra Navrotsky, Arizona State University - Regents Professor at the School of Molecular Sciences
- Prof. James D. Kubicki, University of Texas at El Paso - Professor of Earth, Environmental and Resource Sciences

Additionally, these individuals served on the panel titled “What is Success in the Field of Interfacial Chemistry,” graciously sharing their knowledge as well as personal experiences with success and, just as importantly, challenges in research. The panel proved to be an invaluable opportunity, particularly for early career scientists, as attendees were able to learn as well as recognize tools and traits they possess to also have prolific careers in science.

Team Building Hour

Several networking and community building events were organized as part of the conference, including a memoriam to acknowledge recent passing of colleagues, dinner banquet with the honoree award ceremony, and honoree panel (as mentioned above). Notably, a Team Building Hour on the topic of “Career Resilience” was organized. During the session, led by Prof. Franz Geiger and Prof. Young-Shin Jun, participants shared their challenges, resources, and strategies to thrive in their career development. Key suggestions included reminding oneself of and renewing one’s core values, enhancing adaptability, continuous learning, and increasing efforts for strategic career development, team support, taking initiatives and leadership roles, and acknowledging both challenges and successes.

APPENDIX II: Organizing committee

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Kevin Rosso
Email: kevin.rosso@pnnl.gov
Institution: Pacific Northwest National Laboratory

APPENDIX III: 2025 IEEC Presenters

Monday, May 19, 2025 - Talks

Rachel Segalman | University of California, Santa Barbara

Jenée Cyran | Boise State University

Benjamin Legg | Pacific Northwest National Laboratory

Juliane Weber | Oak Ridge National Laboratory

Benjamin Gilbert | Lawrence Berkeley National Laboratory

Young-Shin Jun | Washington University

Melese Getenet | Lawrence Berkeley National Laboratory

Xinyi Shen | Pacific Northwest National Laboratory

Md Mosfeq Uddin | University of Victoria

Maria Sushko | Pacific Northwest National Laboratory

Anju Gupta | The University of Toledo

Sandra Taylor | Pacific Northwest National Laboratory

Gary Harlow | University of Oregon

Xin Zhang | Pacific Northwest National Laboratory

Krishan Kanhaiya | Ruhr-Universitat Bochum

Yuna Bae | Pacific Northwest National Laboratory

Hilary Emerson | Pacific Northwest National Laboratory

Elias Nakouzi | Pacific Northwest National Laboratory

Nefeli Bompoti | University of Massachusetts Dartmouth

Mingyi Zhang | Pacific Northwest National Laboratory

Marlo Zorman | University of Washington

Monday, May 19, 2025 - Posters

Alejandra Acevedo Montano | Pacific Northwest National Laboratory

Evan Angelo Mondarte | Pacific Northwest National Laboratory

Yang Huang | Pacific Northwest National Laboratory

Ivani Jayalath | University of Mississippi, Pacific Northwest National Laboratory

Md Mosfeq Uddin | University of Victoria

Xiaoxu Li | Pacific Northwest National Laboratory

Winnie Liu | Pacific Northwest National Laboratory

Zsombor Molnar | Pacific Northwest National Laboratory

Lili Liu | Pacific Northwest National Laboratory

Maxime Pouvreau | Pacific Northwest National Laboratory

Soyoung Choi | University of California, Los Angeles

Josiah Wray | Pacific Northwest National Laboratory

Chao Zeng | Pacific Northwest National Laboratory

Samantha Johnson | Colorado School of Mines

Benjamin Jackson | Pacific Northwest National Laboratory

Chenyang Shi | Pacific Northwest National Laboratory

Shuhong Song | Pacific Northwest National Laboratory

Preeti Gahtori | University of Alberta

Ashley Kennedy | Pacific Northwest National Laboratory

John Loring | Pacific Northwest National Laboratory

Ezra Marker | Northwestern University

Alexander von Rueden | Pacific Northwest National Laboratory

Tuesday, May 20, 2025 - Talks

Mischa Bonn | Max Planck Institute for Polymer Research

Simone Pezzotti | ENS, CNRS

Satoshi Nihonyanagi | RIKEN, Japan

Kevin Rosso | Pacific Northwest National Laboratory

R. Kramer Campen | University of Duisburg-Essen

Sara E. Mason | Brookhaven National Laboratory

Raiden Speelman | Northwestern University

Chris Young | Pacific Northwest National Laboratory

Jakob Filser | Boise State University; Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Rebecca Anderson | Oak Ridge National Laboratory

Eric Borguet | Temple University

Mario Villalobos | Universidad Nacional Autónoma de México

Nicole Gonzalez | Northwestern University

Le Wang | Pacific Northwest National Laboratory

Shawn Kathmann | Pacific Northwest National Laboratory

Ying Chen | Pacific Northwest National Laboratory

Hendrik Heinz | University of Colorado Boulder

Ahmet Uysal | Argonne National Laboratory

Juejing Liu | Pacific Northwest National Laboratory

Giovanna Ricchiuti | Pacific Northwest National Laboratory

Sten Lambeets | Pacific Northwest National Laboratory

Kaden Gravois | University of Utah

Tuesday, May 20, 2025 - Posters

Amani Alghamdi | Northwestern University

Jaehun Chun | Pacific Northwest National Laboratory

Wooyong UM | POSTECH

Evan Angelo Mondarte | Pacific Northwest National Laboratory

Jack Grimm | Pacific Northwest National Laboratory

Miguel A Valdes| Pacific Northwest National Laboratory

Ke Yuan | Oak Ridge National Laboratory

Yasmene Elhady | Pacific Northwest National Laboratory

Mal Soon Lee | Pacific Northwest National Laboratory

Dawson Bell | Boise State University

Josephine Hartmann | North Carolina State University

Pedro Josue Hernandez Penagos | University of Texas El Paso

William McLeod | Washington State University

Jueli Shi | Pacific Northwest National Laboratory

Mohammadhasan Dinpajooh | Pacific Northwest National Laboratory

Hoshin Kim | Pacific Northwest National Laboratory

Bruce Palmer | Pacific Northwest National Laboratory

Lorena Tribe| Penn State Berks

Kevin Leung | Sandia National Laboratories

John Loring | Pacific Northwest National Laboratory

Emily Nienhuis | Pacific Northwest National Laboratory

Richa Rashmi | University of California, San Diego

Wednesday, May 21, 2025 - Talks

Francesco Paesani | University of California, San Diego

Damien Laage | Ecole Normale Superieure

Richard Remsing | Rutgers University

Paul Fenter | Argonne National Laboratory

Weitao Liu | Fudan University

Mavis Boamah-Agyemang | Pacific Northwest National Laboratory

Bourgeois Biova Irenee Gadjagboui | Boise State University

Jose Leobardo Banuelos | The University of Texas at El Paso

Franz Geiger | Northwestern University

Duo Song | Pacific Northwest National Laboratory

Dmitry Matyushov | Arizona State University

Eric Tyrode | KTH Royal Institute of Technology

Mohammadhasan (Hadi) Dinpajooh | Pacific Northwest National Laboratory

Kathryn Perrine | Michigan Technological University

Zheming Wang | Pacific Northwest National Laboratory

Piotr Zarzycki | Lawrence Berkeley National Laboratory

Craig Plaisance | Louisiana State University

Mary Jane Shultz | Tufts University

Gregory Schenter | Pacific Northwest National Laboratory

Tarique Anwar | École Polytechnique Fédérale de Lausanne (EPFL)

Collin Smith | University of Oregon

Denis Mulumba | Boise State University

Thursday, May 22, 2025 – Talks

Vicki Grassian| University of California, San Diego

James Kubicki| University of Texas at El Paso

Shaina Kelly| Columbia University

Carolyn Pearce| Pacific Northwest National Laboratory

Chong Liu | University of Chicago

Udo Becker | University of Michigan

Haoyuan Shi | Pacific Northwest National Laboratory

Jacopo Carbone | École Polytechnique Fédérale de Lausanne (EPFL)

Tuan Ho | Sandia National Laboratories

Sarah Saslow | Pacific Northwest National Laboratory

Anastasia Ilgen | Sandia National Laboratories

Seokju Hong | POSTECH

Emily Nienhuis | Pacific Northwest National Laboratory

Sebastien Kerisit | Pacific Northwest National Laboratory

Robert Felsted | Pacific Northwest National Laboratory

APPENDIX IV: Abstract book

MAY 19–23, 2025

Interfaces for Energy and the Environment Conference

HOSTED BY:

PACIFIC NORTHWEST
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RICHLAND, WA

Monday, May 19, 2025 – Abstracts

Topic A: Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies

Monday, May 19th, 2025, 9:10 AM – 11:45 AM PST

Discovery Hall A/B/C

Discussion Leaders: Vicki Grassian (University of California, San Diego), Kevin Rosso (Pacific Northwest National Laboratory)

9:15 AM – 10:00 AM Keynote

Using bio-inspired polymers to understand water-surface interactions

Rachel Segalman[1]

[1]University of California, Santa Barbara

Polypeptoids are non-natural, sequence specific polymers that offer the opportunity to probe the effect of monomer sequence, charge, chirality, and chain shape on interfacial and surface properties. The polypeptoid system allows specific interactions including hydrophobicity and hydrogen bonding to be directly turned on and off and placed at specific locations. In this talk, I will discuss experimental efforts combining controlled peptoid design, dynamic nuclear polarization NMR, and atmospheric XPS studies to understand how specific interactions influence polymer interactions with water and other sorbents. I will also discuss the use of peptoids as highly functional materials ranging from marine anti-fouling coatings to next-generation water purification membranes.

10:15 AM – 10:45 AM Invited

Probing the structure and physicochemical behavior of forever chemicals at aqueous interfaces

Jenée Cyran[1]

[1]Boise State University

Per- and polyfluoroalkyl substances (PFAS) is a prevalent persistent organic pollutant with widespread distribution in the environment and atmosphere. Despite the importance, the fundamental principles of the underlying environmental processing and future outcomes of PFAS remains largely elusive. Here, we probed the behavior of various carbon chain lengths of PFAS and the nonfluorinated alkyl chain versions at the air/water interface utilizing vibrational sum frequency generation (SFG) spectroscopy. We observed an increase in the hydrogen bonded O-H region SFG signal with an increase in chain length for fluorinated alkyl chains, which is the opposite effect for the nonfluorinated chains. These results explore the distinctive physiochemical properties of PFAS with the goal of rational design of remediation techniques for PFAS from the environment.

10:45 AM – 11:15 AM Invited

Charge frustration, surface precipitation and microphase separation at mineral water interfaces

Benjamin Legg,[1] Mingyi Zhang,[1] Zsombor Molnar,[1] Shuhong Song,[1] Christopher J. Mundy,[1] Jim De Yoreo,[1]

[1]Pacific Northwest National Laboratory

Interactions between ions and mineral-water interfaces are of paramount importance in geochemistry. Existing paradigms tend to focus on two major regimes: adsorption of individual ions and heterogenous nucleation of bulk phases, but there is an intermediate regime of 2D surface precipitation that often goes overlooked. Recent studies on the nucleation of hydroxide films have shown a rich array of surface-specific 2D precipitates. Atomic force microscopy (AFM) studies of trivalent cations like Al^{3+}, Fe^{3+}, and Cr^{3+} on mica show that they readily form ordered ion networks (OINs) and nanostructured 2D films. These states are accompanied by significant charge inversions, pointing to a key role of electrostatics. In contrast, divalent cations like Mg^{2+}, Co^{2+}, and Ni^{2+} show much less surface charging, no evidence for OINs, and tend to nucleate continuous films via classical nucleation. Charge frustrated simulations can reproduce both types of behaviors and indicate that the OINs and nanostructured films are examples of microphase separation, driven by a competition between ion clustering and local charge neutrality. These observations motivate the development of new experimental and simulation capabilities to study charged interfaces. These include 3D AFM to map nanoscale surface charge distributions, and simulations to model electrical double layers over heterogeneously charged surfaces. The observation of OINs and microphase separation for many different trivalent cations suggests that these phenomena will be important in diverse environmental settings, and are also likely to influence the behavior of trace metal contaminants and economically elements, such as the lanthanides.

11:15 AM – 11:45 AM Invited

Controls of interfacial reactivity on the direct air caption of carbon dioxide using mineral looping

Juliane Weber,[1] Jacquelyn N. Bracco,[2] Ke Yuan,[1] Nikhil Rampal,[1] Barbara R. Evans,[1] Matthew Boebinger,[1] Albina Y. Borisevich,[1] Elena Tajuelo Rodriguez,[1] Dong Youn Chung,[3] Raphael Hermann,[1] Kevin Rosso,[4] Mavis Boamah,[4] Zheming Wang,[4] Vitalii Starchenko,[1] Lawrence M. Anovitz,[1] Sai Adapa,[1] Gabriela Camacho Meneses,[2] Peng Yang,[1] Jose Banuelos,[5] Andrew G. Stack[1]

[1]Oak Ridge National Laboratory, [2]Queens College, City University of New York, [3]Penn State University, [4]Pacific Northwest National Laboratory, [5]University of Texas at El Paso

The use of alkaline earth oxides for direct air capture in a looped process is a promising technology to potentially remove carbon dioxide from the atmosphere at the gigaton scale. Metal oxides are reacted with ambient air, forming a carbonate, which is then calcined to separate the carbon dioxide and regenerate the sorbent. Current start-up companies mainly utilize CaO due to its fast reactivity, but MgO has potential advantages due to its lower calcination temperature. However, there are knowledge gaps in how relative humidity impacts MgO hydroxylation and carbonation reactions. It is also unclear how impurities, both incorporated and in solution, affect these reactions. Together, these uncertainties limit the application of MgO for direct air capture.

By combining X-ray reflectivity and machine-learning based image analysis of high-resolution electron microscopy images, we determined that higher relative humidity increases hydroxylation and carbonation. Furthermore, we identified that impurities such as iron have very different effects depending on their location: If they are incorporated into the solid, they will slow down both hydroxylation and carbonation reaction and decrease overall carbonation efficiency. *Ab initio* and machine learning potential molecular dynamics simulations indicate that this is due to reduction of surface basicity by leached iron. However, if dissolved iron is present in surrounding solutions during the hydroxylation reaction, carbonation efficiency is increased due to precipitation of nano-scale iron oxides. Our results provide both input for site location selection for direct air capture plants and highlight the importance of sorbents with low iron concentration.

Topic A: Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies

Monday, May 19th, 2025, 1:20 PM – 3:50 PM PST

Discovery Hall A/B/C

Discussion Leaders: Nefeli Bompoti (University of Massachusetts, Dartmoth), Vicki Grassian (University of California San Diego)

1:30 PM – 2:00 PM Invited

Structure and geochemistry of the sulfoxy-terminated pyrite (0001)–water interface at low oxygen partial pressure

Benjamin Gilbert,[1] Anna K Wanhala,[2] Piotr Zarzycki,[1] Sergio Carrero,[1] Michael Whittaker,[1] Slavomir Nemsak,[1] Yarong Qi,[3] Joanne E Stubbs,[4] Peter J Eng[4]

[1]Lawrence Berkeley National Laboratory, [2]Argonne National Laboratory, [3]University of California, Berkeley, [4]University of Chicago

Pyrite (FeS_2) is the most common sulfide mineral on Earth, forming through inorganic reactions in the crust and oceanic hydrothermal systems and via microbially driven processes in anaerobic sediments. The pyrite–water interface is the site of a wide range of adsorption and reaction processes in Earth systems. In particular, pyrite oxidation dramatically affects the geochemistry of surface waters and influences Earth's atmosphere and climate by contributing to the global carbon and oxygen cycles. Mechanistic geochemical models of pyrite interfacial reactivity are limited by the lack of experimentally derived atomistic structures of the reduced and reacting surfaces. Here we reveal the atomic-scale structure of the pyrite (001)—water interface that forms at low oxygen partial pressures relevant to suboxic environments on Earth. The surface is dominantly composed of disulfide groups bound to a single oxygen atom, forming a sulfoxy group that has no known molecular or bulk mineral analog. Surface iron(II) atoms are bound to an adsorbed water molecule and retain their crystal oxidation state. The sulfoxy species is the product of the direct reaction of the surface with the dioxygen molecule. Although it is the product of the first step in the oxidation of pyrite, it can likely form in equilibrium with bulk pyrite in some reducing and acidic solutions. The sulfoxy group is readily protonated through surface acid-base reactions that alter the structure of interfacial water and the free energy of interfacial reactions.

2:00 PM – 2:15 PM

Hydration energies and mechanisms of metal carbonates

Melese Getenet,[1] Piotr Zarzycki,[1] Benjamin Gilbert,[1] Michael Whittaker[1,2]

[1]Energy Geosciences Division, Lawrence Berkeley National Laboratory, [2]Materials Science Division, Lawrence Berkeley National Laboratory

Mineral-water interfaces are critical boundaries influencing geochemical processes such as nucleation, dissolution, and weathering. Nevertheless, the molecular-level understanding of water adsorption on metal carbonate remains incomplete. We employed water adsorption experiments, isosteric heat

calculations, and FTIR spectroscopy to compare the hydration mechanisms of Mg, Mn, and Sr carbonates and microcrystalline versus nanocrystalline calcite. The data reveal surprising variations that point to different compositions and associated reactivities of the carbonate surfaces. For example, water sorption on dry surfaces of calcite and rhodochrosite ($MnCO_3$) is less enthalpically favorable than the heat of water condensation, while water sorption on nanophase calcite is strongly exothermic. Vibrational spectroscopy revealed that the hydration of micro- and nanophase calcite generated free OH species, attributed to water hydrolysis, at different rates and surface coverages. Zeta potential measurements demonstrate that differences in the interfacial properties of partially hydrated micro- and nanophase calcite are preserved in aqueous solution. This work demonstrates that molecular reactions, such as hydration enthalpies and hydrolysis tendency, are strongly coupled to macroscopic properties including sorption thermodynamics and net surface charge. Although aspects of the surface reactivity appear aligned with aspects of the metal geochemistry, including hydration and hydrolysis constants, reactivity trends are more complex. In order to explain and use these findings we seek to develop a metal carbonate surface complexation model spanning all ranges of relative humidity, thin surface water films, and full aqueous solution.

2:15 PM – 2:30 PM

An improved method of characterizing interfacial water at charged aqueous surfaces

Md Mosfeq Uddin,[1] Dennis K. Hore,[1]

[1]Department of Chemistry, University of Victoria

The continued investigation of charge-aqueous interactions is motivated by its fundamental significance in fields such as geology and environmental science for over a century. We have recently demonstrated a technique in which the SFG intensity is collected as a function of the incident angle as a means of separating water contributions from the bonded and diffuse regions of the electrical double layer (JACS, 146, 11756). In that method, we used the angle-dependent variation of the coherence length that affects the diffuse layer as the basis of the analysis. Recognizing that changing the beam angle risks several experimental artifacts, and considering the local field corrections are strongly-angle dependent, a key feature of our technique was that a high ionic strength reference concentration provides a means of performing all necessary corrections empirically, without the need to calculate any correction factors. When using this method to normalize the data, features related to the interfacial and diffuse layer contributions are immediately revealed. However, a shortcoming was that, by analyzing only the ratio with respect to the high ionic strength, the scale was lost and only changes that manifest themselves in the shape of the |χ(2)total| vs angle curves could be analyzed. We now improve this method by determining the absolute scale of |χ(2)total| in addition to performing the empirical angle-dependent corrections at high ionic strength. We illustrate that this permits us to solve for the complex-valued bonded χ(2) response and the interfacial potential simultaneously.

2:50 PM – 3:20 PM

Advancing thermal management and water purification technologies via nature-inspired interfacial engineering

Anju Gupta[1]

[1]University of Toledo

Nature-inspired interfacial engineering offers a transformative approach to designing functional materials with tunable properties, addressing critical challenges in energy, environment, and healthcare in the Anthropocene era. Our research bridges the gap between material design and transport phenomena, opening new avenues for innovative solutions in thermal management and water treatment technologies. By leveraging process-structure-property correlations, we tailor advanced interfaces with tunable wettability and porosity to enhance thermal and fluid transport. Using magnetically aligned metal links, we engineer interfaces that significantly improve heat transfer efficiency. Our 2D magnetically aligned Metal Organic Deposition (MOD) ink-based surfaces have demonstrated substantial increases in heat transfer coefficients and faster onset of nucleate boiling, offering promising advancements for next-generation cooling solutions. Complementing these thermal innovations, we have developed mixed matrix membranes through a bottom-up approach that show remarkable improvements in water vapor flux and salt rejection rates, even with minimal nanomaterial loading for enhancing desalination processes. Beyond material development, our research advances the fundamental understanding of multiphase transport phenomena, including insights into nucleation, bubble dynamics, and capillary-driven flows in hierarchical structures. This talk will present our latest findings and discuss their implications for creating more efficient and sustainable technologies in thermal management and water purification.

2:50 PM – 3:20 PM

Cation effects on solvent entropy and charge transfer processes at Au(111) electrodes

Gary Harlow,[1] " Ziyan Yang,[1] Collin Smith,[1]

[1]University of Oregon

This study investigates the influence of alkali metal cations (K^+, Na^+, Li^+, and Cs^+) on the electrosorption of chloride ions (Cl-) at a Au(111) single crystal electrode. Specifically, we focus on the electrosorption valency of Cl-, which reflects the degree of charge transfer during adsorption, and how it varies with the cation identity. Furthermore, we examine the impact of these cations on the potential of maximum entropy (PME) of water at the electrode-electrolyte interface. The PME, determined using laser-induced temperature jump spectroscopy, signifies the potential at which water exhibits the highest degree of orientational disorder. Our findings provide insights into how different cations modify the interfacial water structure and consequently influence the electrochemical behavior of the system.

3:35 PM – 3:50 PM

Polarizable model of graphitic materials and its applications to nanotechnology

Krishan Kanhaiya,[1] Hendrik Heinz,[2] Marialore Sulpizi,[1]

[1]Ruhr-Univerität Bochum, [2]University of Colorado Boulder

Graphitic materials are of significant importance in the research and industrial community due to their tunable electrical conductivity, band gap, thermal property and high strength to mass ratio. They are used in battery or fuel cells as electrodes, refractory material, lubricant, in nuclear reactors, aerospace, water purification, steelmaking and bio-sensing. In this work we present a realistic, all-atom polarizable model of graphite with flexible dummy electrons to model the polarizable nature of electron cloud in graphitic structures (graphene, graphite and carbon nanotubes) in a similar way to the approach which we have used in the past to describe image charge effects for ions approaching gold metal surfaces. The models predict density, lattice parameters, surface energy, hydration energy, water contact angle and elastic constants within 1%, 1%, 5%, 5%, 5% and ~10 % respectively as per the Interface Force Field protocol. Additionally, the model also reproduces experimental and DFT data on binding energies and profiles for cations, anions and neutral molecules (water and amino acids). We also discuss the frictional behavior at the interface with water which is improved significantly with respect to previous classical models. An accurate description of interfacial friction is of key relevance to design improved materials and devices for water desalination and electric energy from salinity gradient in two different electrolyte solutions (blue energy).

4:10 PM – 4:40 PM Invited

Advancing subsurface monitoring: Spectral induced polarization for detecting remedial amendment-induced changes at the solid-water interface

Hilary Emerson,[1] Zoe Vincent,[1] Jonathan N. Thomle,[1] Chao Zeng,[1]

[1]Pacific Northwest National Laboratory

Noninvasive geophysical methods can monitor extensive subsurface volumes with relatively high spatial resolution, offering indirect measures of solution and surface processes. Complex conductivity measured via spectral induced polarization (SIP) may be able to distinguish changes in solution conductivity from surface conductivity and polarization caused by biogeochemical reactions (such as adsorption, precipitation, redox, and biofilm growth) that modify surface properties, like surface area, grain size, as well as surface chemistry by influencing ion movement within the electrical double layer. Here, laboratory-scale, one-dimensional columns evaluated remedial amendment delivery and subsequent reactivity with SIP. Results are compared for conducting amendments, zero valent iron (ZVI) and sulfur modified iron (SMI), and insulating amendments like apatite, both of which are frequently used for sequestration of inorganic contaminants in the subsurface.

The greatest sensitivity in SIP was observed for conducting amendments, including zero valent iron and sulfur modified iron, with significant shifts in both magnitude and frequency of the response during extended corrosion. Initially, the magnitude of polarization increased and later decreased, likely due to early formation of highly conductive Fe(II) oxide phases on the surface, followed by their oxidation to less polarizable Fe(III) oxides and hydroxides. Frequency shifts were also observed, possibly due to changes in surface area, surface roughness, and pore spaces. Interestingly, shifts were detected even

during formation of non-conducting phases like apatite with an increase in imaginary conductivity attributed to changes in mineral surfaces. However, the polarization magnitude was heavily influenced by solution ionic strength, as anticipated during formation of insulating phases.

4:40 PM – 4:55 PM

Investigating PFOS-surface interactions across scales: Implications for reactive transport modeling and applications

Nefeli Bompoti,[1] Zoi Dokou,[2] Devin Farrell,[3]

[1]University of Massachusetts Dartmouth, [2]California State University, Sacramento, [3]Goldman Environmental Consultants, Inc.

Per- and polyfluoroalkyl substances (PFAS) comprise a diverse group of persistent environmental contaminants, which have been extensively employed across various industrial and commercial applications over the past six decades. Among the most concerning sources of PFAS contamination are Aqueous Film-Forming Foams (AFFFs), which mainly contain Perfluorooctane Sulfonate (PFOS), were commonly used by firefighters during training exercises. When combined with natural rainfall, these foams contribute to the infiltration of PFAS compounds into groundwater aquifers.

Although several studies have explored the fate and transport of PFAS in both laboratory settings and real-world impacted sites, research on the specific interactions between interfacial PFOS and mineral surfaces remains limited. This study aims to fill this gap by investigating the adsorption of PFOS on 2-line ferrihydrite, ferrihydrite-coated sand, and soil samples obtained from a PFOS-contaminated site in Southern New England. Batch adsorption experiments, coupled with surface complexation modeling (SCM), are employed to gain insights into the reactive transport behavior of PFOS under varying geochemical conditions. The results suggest that PFOS adsorption onto ferrihydrite-coated sand and soil is primarily driven by retention mechanisms associated with the ferrihydrite and quartz surfaces. The SCM model developed in this study highlights the significant role of pH-dependent adsorption, driven by the surface charge of ferrihydrite, alongside non-electrostatic, hydrophobic interactions with quartz surfaces using the component additivity approach. These findings are further linked to traditional partitioning coefficients (Kds), providing valuable insights into the implications for field transport modeling applications and enhancing our understanding of PFOS migration in contaminated environments.

4:55 PM – 5:10 PM

Advancing our interpretation of spectral induced polarization signatures in microporous media using Brownian dynamics simulations

Thomas Underwood,[1] Kevin M. Russo[1]

[1]Pacific Northwest National Laboratory

Spectral Induced Polarization (SIP) spectroscopy is a burgeoning geophysical technique that applies a low-frequency electric field (<MHz) to a soil or rock sample to collect complex impedance spectra. It is a nondestructive characterization method that can, in principle, provide information on the mineralogical composition, water content, and the pore-water chemistry of a sample. Despite its promise, SIP spectra are often difficult to deconvolute, especially in the low-frequency regime.

In this regime, theory suggests that the SIP response arises from polarization and relaxation of ions in electrical double layers at mineral/water interfaces lining the electrically connected pore network structure. It is a phenomenon rooted in potentially useful molecular scale properties, but resolves on the timescale of seconds, and poses a difficult task to examine using current modeling and experimental techniques.

To address this gap, we have developed an efficient computational model of ionic diffusion in porous media based upon the Brownian dynamics description of charge carriers. We examine the properties of ionic diffusion and the subsequent polarization relaxation in model slit pore geometries, as well as increasingly complex pore-geometry networks.

Our model offers an opportunity to shed light on mechanisms giving rise to the low-frequency SIP response with near molecular-level resolution. Through planned comparison with measurements on well-defined model porous media we aim to ultimately understand how impedance spectra relate to the interfacial chemical properties of a sample as well as its pore-network geometry.

Topic B: Abiotic and biologically-mediated nucleation, growth and dissolution

Monday, May 19th, 2025, 1:20 PM – 5:10 PM PST

Discovery Hall D/E

Discussion Leaders: James De Yoreo (Pacific Northwest National Laboratory), Young-Shin Jun (Washington University)

1:30 PM – 2:00 PM Invited

Nucleation-controlled critical element recovery and carbon mineralization

Young-Shin Jun,[1] Xueyi Liu,[1] Jennifer Houghton,[1] Zoltan Vaci,[1] David Fike[1]

[1]Washington University

Resilience in both climate and critical elemental supply is essential for our sustainable society. During the clean energy transition, the demand for critical elements, such as cobalt, is increasing. Therefore, it is vital to address both carbon management and the recovery of critical elements from low-grade ores simultaneously. In this study, we examined the formation of metal carbonate structures from mixed metal ion solutions that mimic the leached solutions from mafic and ultramafic low-grade ores. We discovered that cobalt carbonate nucleation occurs first, forming a core, followed by magnesium carbonate forming a shell around the cobalt carbonate core. This core-shell carbonate formation is attributed to differences in nucleation kinetics and heteroepitaxial relationships. Because of the lattice differences, the shell structure develops nanochannels, which facilitate the effective transport of reactive fluids. When sulfide ions are introduced, only the cobalt carbonate dissolves and then nucleated as cobalt sulfide within the core and nanochannels, while the magnesium carbonate remains intact. This unique core-shell structure, combined with selective nucleation and dissolution, enables effective recovery of cobalt, while magnesium carbonate can durably store CO_2. This novel process shows great promise for the concurrent recovery of critical elements and carbon mineralization.

2:00 PM – 2:15 PM

Impact of interfacial structure on heterogeneous nucleation of amorphous carbonates

Xinyi Shen,[1] Micah P. Prange,[1] Sebastien N. Kerisit[1]

[1]Pacific Northwest National Laboratory

Carbonation reactions are both a key pathway to CO_2 sequestration and a potential extraction or pre-treatment method for the recovery of critical elements (CE), such as nickel and cobalt, from mafic and ultramafic low-grade ores. Mafic and ultramafic silicates, such as olivine, are highly reactive to carbonation. However, our understanding of the nucleation of secondary minerals during carbonation, their ability to incorporate CE, and the physical and chemical processes during silicate carbonation remains limited.

We performed molecular dynamics (MD) simulations of amorphous carbonate nucleation on silicate surfaces. Carbonates often nucleate as amorphous intermediates to crystalline end products. A first series of MD simulations focused on the impact of surface structure on heterogeneous nucleation of amorphous carbonates. We constructed interfacial systems of amorphous calcium ($CaCO_3 \cdot H_2O$, ACC) and magnesium carbonate ($MgCO_3 \cdot H_2O$, AMC) nuclei in contact with three hydroxylated α-quartz (SiO_2) surfaces. A second series of MD simulations examined the heterogeneous nucleation of AMC on forsterite (Mg_2SiO_4) and amorphous silica (SiO_2) as model systems of pristine and fully-reacted silicate surfaces, respectively. The simulations showed silicate surfaces drew water molecules out of the carbonate nuclei to form a partial hydration layer. Because of this partial hydration layer and its disruption to the ACC/AMC structure, interfacial energy calculations predicted homogeneous nucleation of ACC/AMC to be favored over heterogeneous nucleation. The MD simulations hence provided an atomic-level explanation for a reported nonclassical growth mechanism whereby carbonate minerals grow via homogeneous nucleation and subsequent surface attachment of amorphous intermediate.

2:15 PM – 2:30 PM

Role of dynamic polarization interactions in the electrical double layer at mineral interfaces with electrolyte

Maria Sushko,[1] Duo Song,[1] Eric Bylaska,[1] Kevin Rosso,[1] Lili Liu,[1] Andrew Ritchhart[1]

[1]Pacific Northwest National Laboratory

Reactions at mineral interfaces with aqueous solutions control many geochemical and biogeochemical processes in the Earth’s critical zone. At the molecular level, insights into important properties such as the structure of the electrical double layer (EDL) at specific mineral interfaces continue to improve due to the increasing fidelity of laboratory instrumentation and computational approaches. However, molecular simulation approaches suffer from limited reach into relevant scales of time, length, and system complexity. To span this gap, a novel hybrid approach that couples first-principle plane-wave density functional theory (DFT) with classical DFT (cDFT) is demonstrated and applied to calcite (104) interfaces with various electrolytes. In this approach, a region of interest described using DFT interacts with the surrounding medium described using cDFT to arrive at a self-consistent ground state. Benchmarking against experimental observations and entirely first-principle DFT simulations demonstrates that this hybrid model efficiently encompasses the key short-range and collective interactions in the EDL. Benchmark simulations of calcite (104)/solution interfaces reveal the key static and dynamic polarization interactions that give rise to structuring of ions and water. This new ability to efficiently and rigorously predict EDL structure at mineral surfaces in contact with complex solutions paves the way to accurately modeling sorption, nucleation, dissolution, and growth in realistic systems. Notable examples of polarization interactions exerting morphological control of mineral growth will be discussed.

2:50 PM – 3:20 PM Invited

Facet-dependent growth and dissolution of hematite during autocatalytic reactions with Fe(II) and oxalic acid

Sandra Taylor,[1] John Cliff,[1,2] Kevin Rosso[1]

[1]Pacific Northwest National Laboratory, [2]Oak Ride National Laboratory

The autocatalytic redox interaction between aqueous Fe(II) and Fe(III)-(oxyhydr)oxide minerals in the presence of organic chelating ligands can lead to accelerated rates of dissolution and/or recrystallization via coupled dissolution and growth between specific facets/sites. Direct insight into these mass transport processes and pathways during mineral recrystallization however remain poorly understood due to challenges monitoring the flux of iron atoms from the solution to the solid phase as well as between solid interfaces. Here, we studied competitive growth and/or dissolution processes across well-faceted hematite crystallites reacting with Fe(II) and/or oxalic acid. A variety of techniques were utilized to effectively follow mass transport in the solution and solid phases, including spectrometric, microscopic, and isotopic tracers coupled with mass-sensitive imaging techniques. We clearly demonstrate that Fe(II) oxidative adsorption can occur on (001) and (012) surfaces in the absence of oxalate, but when oxalate is present selective dissolution of the (001) surface prevails. Comparison between particle micro topographies following reaction with Fe(II), oxalate, and Fe(II)-oxalate also show substantially different behavior, consistent with distinct mechanisms of interaction with hematite surfaces. Ultimately, this study presents new insight and approaches for distinguishing crystal growth, dissolution, and recrystallization processes. These results also demonstrate substantial anisotropy in the interfacial reactivity of iron oxide materials, which is important to assessing and predicting their effectiveness as catalysts across various environmental processes.

3:20 PM – 3:35 PM

Understanding particle-mediated growth pathways by using advanced microscopy techniques

Xin Zhang,[1] Xiaoxu Li,[1] Maria Sushko,[1] Jim De Yoreo,[1] Kevin M. Rosso[1]

[1]Pacific Northwest National Laboratory

Particle aggregation, including the phenomenon of oriented attachment (OA), where crystalline particles join via specific crystal faces with lattice matching, is a key mechanism in crystal growth. This process plays a critical role in developing hierarchically structured materials for catalysis, energy storage, and medicine. Using advanced transmission electron microscopy (TEM) and computational methods, we investigate OA mechanisms in metal oxide systems and their relationship to interfacial structure in vacuum and water vapor. First, we explore hematite nanocrystals with different facets ({001}, {012}, {104}, {116}) using high-resolution TEM. Results show aggregation-driven crystallization is orientation-dependent (along [001]) and not reliant on exposed facets. Density functional theory (DFT) links these behaviors to surface interactions. Second, the formation of gibbsite mesocrystals is explored. Monodisperse gibbsite nanoplates (~100 nm) form hexagonal columnar mesocrystals (~100 μm) upon water evaporation. Small-angle X-ray scattering/wide-angle X-ray scattering (SAXS/WAXS) and X-ray diffraction (XRD) confirm well-aligned particles along specific zones. *In situ* liquid-phase TEM reveals OA of gibbsite nanoplates, consistent with *ex situ* results. Molecular dynamics (MD) simulations indicate a lower energy barrier for sliding along the (010) direction (0.89 kcal/mol) than (100) (2.49 kcal/mol).

Third, anisotropic forces between rutile TiO_2 (001) nanocrystals are measured using environmental TEM-atomic force microscope (AFM). Attractive forces depend on azimuthal alignment and hydration, aligning with Lifshitz theory predictions and demonstrating dispersion forces' role in particle alignment.

3:35 PM – 3:50 PM

Dynamic surface potential induced by competitive ion adsorption switches particle-attaching facets

Yuna Bae,[1] Eun Mi Kim,[2] Jaehun Chun,[1] Kristen Fichthorn,[2] Jim De Yoreo,[1] Dongsheng Li[1]

[1]Pacific Northwest National Laboratory, [2]The Pennsylvania State University

The mechanism of facet selectivity during crystal growth by oriented attachment (OA) and its dependence on the structure and chemistry of the NP-electrolyte interface are poorly understood phenomena of mineral-fluid systems. The electrostatic forces associated with the facet-dependent surface charge is of NPs is expected to play a role, but whether — or when — it dominates over other factors, like hydration barriers or van der Waals interactions, is unclear. Here we investigate the formation of branched cubic Pt mesocrystals through OA in electrolyte solutions using advanced *in situ* imaging, surface characterization, and theoretical and computational modeling. We find that mesocrystal formation begins with aggregation of the NPs into a disorganized cluster within which subsequent OA events occur. During this process, the NPs are initially spatially separated in the clusters and become crystallographically coaligned before attachment. Attachment begins on the {100} facets of the inner particles, forming a cubic core, and later shifts to the {111} facets, leading to the growth of branched rods on the faces of cube. The transition from {100} to {111} attachments is driven by competitive ion adsorption and the resulting evolution of surface potential. This study demonstrates that anisotropic electrostatic interactions and resultant torques govern the directionality of OA, providing a deeper insight into how solution chemistry influences nanomaterial assembly and valuable guidance for designing complex nanostructures with tailored properties for diverse applications.

4:10 PM – 4:40 PM Invited

Interfacial solution structure impacts particle aggregation, ice nucleation, and incorporation of nanoparticles in growing crystals

Elias Nakouzi,[1] Mingyi Zhang,[1] Pravalika Butreddy,[1] Jaeyoung Heo,[1] Philip Brahana,[2] Victorien J. Bernat,[3] Bhuvnesh Bharti,[2] Jaehun Chun,[1] Ulrich B. Wiesner,[3] Lara A. Estroff[3]

[1]Pacific Northwest National Laboratory, [2]Louisiana State University, [3]Cornell University

Solution structure at solid-liquid interfaces creates inter-particle forces and chemical potential gradients that influence particle stability, reactivity, and aggregation. However, despite this relevance to a variety of research fields, significant knowledge gaps remain in our understanding of solid-liquid interfaces at the molecular scale. Using a combination of atomic force microscopy, confocal fluorescence microscopy, colloidal theory, and atomistic simulations, we present three case studies examining the effect of interfacial solution structure on particle aggregation, crystal growth, and heterogeneous nucleation. Firstly, we determined that extreme salt concentrations enhance ion correlations at the surface of boehmite nanoparticles, resulting in strong repulsive forces at short particle separations that decrease the rate of particle aggregation. In the second study, we investigated the incorporation of ligand-coated nanoparticles in growing calcite crystals. This process is governed by the interactions experienced by an incoming particle as it penetrates the interfacial hydration layers, as well as the binding energy upon adsorption to the growing crystal surface. Thirdly, we determined that oxidizing a polymer surface results in the assembly of hydration layers at the polymer-water interface, which increase the surface hydrophilicity and the propensity for nucleating ice. We anticipate that these studies will provide insights into the molecular nature of solid-liquid interfaces with important implications on relevant problems in geochemistry, electrochemistry, and materials synthesis.

4:40 PM – 4:55 PM

Driving forces for the incorporation of nanoparticles within growing single crystals

Mingyi Zhang,[1] Victorien J. Bernat,[2] Kuan-Ting Liu,[2] Nada Naguib,[2] Ulrich B. Wiesner,[2] Lara A. Estroff,[2] Elias Nakouzi[1]

[1]Pacific Northwest National Laboratory, [2]Cornell University

Nature's ability to create hybrid biomolecular-inorganic materials by incorporating organic components into inorganic matrices results in biogenic minerals with a remarkable synergy of strength and toughness, often surpassing their geological counterparts. However, the mechanisms underlying the formation of these bio-hybrid materials remain poorly understood, largely due to the complexity of organic-inorganic interfacial interactions. Previous research has shown that ultrasmall, sub-10 nm PEGylated silica nanoparticles, known as Cornell prime dots (C′ dots), can be incorporated into single calcite crystals to form hybrid structures. Here, we explore the initial stages and mechanisms of nanoparticle incorporation into calcite. We utilize 3D Atomic Force Microscopy (3D AFM) to probe solution structure and hydration forces, Dynamic Force Spectroscopy (DFS) to measure binding energy, and confocal fluorescence microscopy to quantify nanoparticle incorporation. Mimicking C′ dots, we functionalize silicon AFM tips with a PEG shell and various functional groups, including hydroxyl, amine, and carboxyl, using silane and click chemistries. Compared to a bare PEG probe, hydroxyl groups lower hydration forces, reducing kinetic barriers, carboxyl groups increase binding energy, and amine groups exhibit dual functions. Monte Carlo simulations show that hydration forces impact collision frequency, and the binding energy determines the particle's surface lifetime, both crucial for successful incorporation. The results here provide insights into the organic-mineral interfacial structure and suggest design principles for next-generation organic nanoparticles, paving the way for advanced materials engineering.

4:55 PM – 5:10 PM

Molecular informed frustrated charge models for speciation and nucleation of electrolytes

Marlo Zorman,[1] Christopher J. Mundy,[2] Harley Pyles,[3] David Baker[4]

[1]Department of Molecular Engineering, University of Washington, [2]Department of Chemical Engineering, University of Washington, [3]Institute for Protein Design, University of Washington, [4]Department of Biochemistry, University of Washington

Nucleation is the process by which particles aggregate into crystalline-like solids. It is ubiquitous in nature and a common initiating step in first-order phase transitions, making it highly interesting both as a subject of fundamental studies and in applications research. However, computational studies of nucleation are challenging due to the time and size scales involved. In this work, we introduce a self-consistent multiscale framework for the simulation of nucleation at physiological concentrations that overcomes these limitations. A continuum and a lattice-based Monte Carlo are each embedded with all-atom derived pairwise potentials, enabling reconstitution into all-atom Molecular Dynamics simulations. The lattice model further incorporates a novel full Ewald summation for electrostatics, providing high precision in modeling long-range interactions. We demonstrate that this framework accurately predicts speciation distributions and nucleation rates for NaCl and $CaCO_3$ at physiological concentrations. Finally, we extend the model to investigate the design of de novo biomimetic mineralizing proteins, providing a roadmap for their rational design through a combination of physical principles and machine learning.

Posters

Poster flash talks

Monday, May 19th, 2025, 1:00 PM – 1:20 PM PST

Discovery Hall Horizon ABC

Moderator: Sarah Saslow (Pacific Northwest National Laboratory)

Poster session

Monday, May 19th, 2025, 5:10 PM – 7:00 PM PST

Discovery Hall Horizon ABC

**Poster abstracts are grouped by topic

Abiotic and biologically-mediated nucleation, growth and dissolution

Nickel hydroxide–nickel carbonate competitive growth on carbonate surfaces

Winnie Liu,[1] Nabajit Lahiri,[1] Sebastian Mergelsberg, [1] Shawn Riechers, [1] John Loring, [1] Mark Bowden, [1] Sebastien Kerisit.[1]

[1]Pacific Northwest National Laboratory

The thermodynamic and kinetic factors controlling the competitive heterogeneous nucleation and growth of ubiquitous metal carbonate and hydroxide phases are poorly understood. In this work, calcite ($CaCO_3$) and magnesite ($MgCO_3$) powders reacted with $NiCl_2$ solutions at 22 °C and 5 °C. Ni is at the same time a micronutrient, a contaminant, and a critical element to the world's economy, and its fate and transport are thus of significant interest. Evidence from X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, and energy-dispersive X-ray spectroscopy pointed to the formation of mixed Ni carbonate-Ni hydroxide amorphous surface precipitates. On calcite, XPS detected primarily $Ni(OH)_2$ despite the initial solutions being more supersaturated with respect to gaspéite ($NiCO_3$) than to theophrastite ($Ni(OH)_2$) by a factor of 17–18. In contrast, $NiCO_3$ was the dominant component detected by XPS on magnesite in the same conditions. Decreasing the temperature had the effect of increasing the proportion of $NiCO_3$ to the detriment of $Ni(OH)_2$. The experimental observations were consistent with low lattice/cation size mismatch favoring $NiCO_3$ nucleation and temperature most influencing $Ni(OH)_2$ nucleation. Comparison to previous work on Co-reacted powders indicated the differences in lattice/cation size mismatch and/or water exchange rate impacted the composition of the surface precipitates more than the relative thermodynamic stabilities of the competing minerals. This work sheds light on the factors that control the competition between surface precipitates and contributes to efforts toward understanding and predicting the fate and transport of Ni in geochemical systems.

Mineral dissolution by polymeric complexes

Xiaoxu Li,[1] Qing Guo,[2] Yatong Zhao,[1] Chang Qian,[3] Maxime Pouvreau,[1] Trenton R Graham,[1] Qian Chen,[3] Aurora E. Clark,[2] Kevin M. Rosso,[1] Xin Zhang[1]

[1]Pacific Northwest National Laboratory, [2]The University of Utah, [3]University of Illinois at Urbana−Champaign

Mineral dissolution is a fundamental interfacial process with broad relevance across materials science, earth sciences, and pharmaceutics. Mineral dissolution is typically thought to occur by the detachment of monomeric building blocks of the crystal structure, although direct evidence is rare. Using *in situ* high-speed atomic force microscopy to examine step-edge retreat dynamics at high resolution, we report that the dissolution of gibbsite in alkaline solutions occurs mainly by the release of aluminate dimers, which subsequently dissociate into the monomeric species that dominate the solution. The observed dissolution anisotropy is readily explained by this mechanism, which was further supported by density functional tight-binding simulations of detachment activation energies. Recognition that such polynuclear dissolution mechanisms exist may enable an improved understanding of processes regulating mineral dissolution rates in nature and industry.

The adsorption of rare earth element ions onto the surface of gibbsite nanoparticles

Zsombor Molnar,[1] Benjamin A. Legg[1]

[1]Pacific Northwest National Laboratory

Sedimentary rare earth element (REE) deposits are one of the most important sources of REE metals due to their easy accessibility and relatively low cost of extraction. In these deposits, the trivalent REE ions are typically adsorbed on the charged surfaces of different minerals such as gibbsite or phyllosilicate clay minerals. Recent studies on the interaction between trivalent metal cations and mineral surfaces revealed that the charged surfaces could attract and adsorb ions thus enhancing the formation and the stabilization of novel, quasi-two-dimensional surface phases. We hypothesize that these phenomena are also important for the behavior of REE ions and the formation of different REE minerals, and that environmental parameters such as pH and dissolved carbonate ions may affect these interactions. We studied the effect of pH, atmospheric CO_2 and dissolved REE ion concentration on the surface charges of laboratory synthetized gibbsite nanoparticles using a dynamic light scattering (DLS) instrument connected to an auto-titrator. We correlated these results with scanning transmission electron microscopy imaging used to confirm the presence of REE ions on the surface of gibbsite. Our results show that the REE ions affected the surface potentials of gibbsite indicating adsorption processes possibly via surface complexation processes and promoted the aggregation of nanoparticles. However, the presence of different carbonate species that originate from atmospheric CO_2 decreased the ζ potential of gibbsite particles, especially at higher pH, thus modifying its cation adsorption capabilities and the behavior of REE ions.

Epitaxial growth of 2D core-crown SnS_2/$SnSe_2$ heterostructure through interfacial modification with polyvinylpyrrolidone

Lili Liu,[1] Duo Song,[1] Mitchell E. Kaiser,[1] Jun Liu,[1] James J. De Yoreo,[1] Maria L. Sushko[1]

[1]Pacific Northwest National Laboratory

Developing generalized strategies for controlled synthesis of 2D heterostructures remains a significant challenge because the existing approaches often suffer from poor reproducibility and scalability. In this study, a solution synthesis approach for epitaxial core-crown heterostructures with controlled band alignment, that overcomes these challenges is reported. Polyvinylpyrrolidone (PVP) is used as a structure-directing agent to reduce lattice mismatch between SnS_2 and $SnSe_2$ (10-10) surfaces and direct epitaxial growth of $SnSe_2$ crown on SnS_2 seed. Additionally, PVP adsorption to the basal plane prevents van der Waals stacking and stabilizes 2D heterostructures during synthesis. Driven by interfacial thermodynamics, the formation of the core-crown heterostructure is highly reproducible and the size of the 2D heterostructure and relative areas of the core and the crown can be precisely controlled in a two-step process by varying synthesis times for the seed and the crown. The identified growth pathway for 2D heterostructures can be generalized to other combinations of van der Waals materials to provide a platform for synthesizing micron-size epitaxial heterostructures with a desired electronic structure for catalysis and microelectronics.

Emerging applications and tools for energy challenges

Assessing electrochemical interfacial properties in porous media for energy storage

Chao Zeng,[1] Soowhan Kim,[1] Yucheng Fu,[1] Yunxiang Chen,[1] Jie Bao,[1] Zhijie Xu[1]

[1]Pacific Northwest National Laboratory

The monitoring of interfacial properties under electrochemical conditions is pivotal for optimizing energy storage systems. In these systems, interfacial changes are governed by faradaic reactions and electrochemical double-layer capacitance as redox reactions occur at the solid-aqueous interface. Electrochemical impedance spectroscopy (EIS) offers a convenient in-situ method to track resistance changes in porous media. However, interpreting EIS data to accurately derive interfacial properties poses significant challenges. This study introduces a novel analytical approach for interpreting spatially distributed interfacial properties. Using a redox flow battery as a case study, we demonstrate the robust application of this method. Our findings successfully correlate microscale interfacial parameters with macroscopic measurement signals, advancing understanding and capability in electrochemical system analysis.

Separation of rare earth elements in confined amine-functionalized graphene oxide membranes

Josiah Wray,[1] Karim Garciayala,[1] Oliva M. Primera-Pedrozo,[1] Difan Zhang,[1] Venkateshkumar Prabhakaran,[1] Manh-Thuong Nguyen,[1] Grant E. Johnson[1]

[1]Pacific Northwest National Laboratory

Selective separation of critical materials from domestic feedstocks, such as produced water and recycled electronics, is essential for economic growth, national security, and environmental remediation. Understanding the interactions between solvated ions and solid interfaces is essential for advancing energy- and atom-efficient separations. Graphene oxide (GO) membranes are known to filter ions based on their size and charge. This control over the filtration process makes GO attractive for critical mineral recovery and water purification. Nevertheless, tuning GO membranes for separations remains challenging due to the limited understanding of how functional groups influence ion adsorption and water permeation in confined transport channels. Introducing nitrogen groups into GO through reactions with carboxylic acids leads to the formation of amide bonds. This functionalization enhances selective ion permeation rates by altering the surface charge and hydrophobicity of the membranes, allowing for better selectivity. Herein, amine-functionalized GO laminates were synthesized and evaluated for the separation of rare earth elements. Ion permeation experiments were performed using model feedstock solutions of individual metal chloride salts. Changes in conductivity were monitored electrochemically, which enabled the quantification of cation transport across the membranes. Amine interactions with GO and solvated metal cations were determined using Fourier transform infrared spectroscopy, and the surface charge of the materials was characterized using zeta and streaming potential measurements. This study provides insight into how amide bond formation impacts the selective separation of rare earth elements using GO membranes. The findings underscore the importance of understanding molecular interactions at confined solid-liquid interfaces for designing effective separations.

Investigation of mineral-water-CO_2 reactions at interfaces for carbon storage mitigating climate change

Soyoung Choi,[1] Ah-Hyung Alissa Park,[1] Aaron Moment,[1] Quin Miller,[2] Todd Schaef[2]

[1]University of California, Los Angeles, [2]Pacific Northwest National Laboratory

Geological formations such as basalt and peridotite rocks are promising hosts for carbon dioxide storage, offering a sustainable pathway to mitigate climate change due to their abundance and high reactivity with CO_2. These formations exhibit complex mineral phases that critically influence the transport and thermodynamic behaviors of chemical reactions at the mineral-aqueous interface. Understanding the interplay between mineralogical complexities and fluid chemistry is essential to engineering efficient carbon sequestration processes within these geological settings.

This study provides an in-depth investigation into the dissolution, nucleation, and carbonation reactions occurring during geological carbon mineralization. To the best of our knowledge, this work uniquely explores the effects of a wide pH range, alongside other parameters such as alkalinity, temperature, and fluid chemistry, on interfacial transport and reaction behaviors. To address the role of mineralogical heterogeneity, we analyzed samples ranging from homogeneous minerals to complex rocks, including novel peridotite specimens collected from Tamarack, Minnesota.

To monitor the dynamic evolution of carbonation products and surface transformations, we integrated advanced spectroscopic, thermogravimetric, and microscopic techniques. Complementary geochemical modeling was employed to elucidate reaction pathways and mechanisms governing interfacial processes. The findings from this study enhance the fundamental understanding of mineral-water-CO_2 reactions at interfaces across diverse conditions, providing critical insights for engineering and optimizing carbon sequestration strategies and advancing environmental applications in geological formations.

Frontiers in computation and advances in analytical techniques

Accurate computational prediction of the acidity constants of lanthanides

Maxime Pouvreau,[1] Christopher J. Mundy,[1] Benjamin A. Legg[1]

[1]Pacific Northwest National Laboratory

Lanthanides, part of rare earth elements, exhibit increasing contraction with increasing atomic number, leading overall to an increase in complexation and acidity constants and a decrease in solubility constants. However, their chemistry near mineral interfaces, including selective nucleation with potential environmental significance, is poorly understood. The precipitation of lanthanide hydroxides first necessitates hydrolysis of the aqua Ln^{3+} cations, and recent work has demonstrated that the acidity constants of metal cations can be affected by their interaction with surfaces. Since a molecular-level understanding of the influence of metal cation-surface interactions on reactivity is very challenging to achieve experimentally, simulations are essential.

A necessary first step is to establish an appropriate *ab initio* molecular dynamics (AIMD) methodology, starting with the more approachable bulk solution hydrolysis. pK_a changes across the series are subtle and an accurate treatment of electron correlation in f-block elements requires moving beyond pure GGA DFT functionals commonly used in AIMD. In this work, we employed hybrid DFT in conjunction with new basis sets and pseudopotentials. Two AIMD-based computational protocols for obtaining pK_as—direct proton transfer via reaction coordinate biasing and indirect transfer through the proton insertion/deletion method—were utilized. Thermodynamic cycles ensured consistency in relating simulation outputs to standard-state free energies, addressing limitations in earlier work. This framework allows for robust predictions of the acidity of lanthanides in solution and lays the groundwork for future studies on their reactivity near mineral surfaces.

Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies

Investigation of coupled proton-electron-mediated extraction of rare earth elements at polyoxometalate-functionalized electrodes

Alejandra C. Acevedo Montano,[1] Yang Huang,[1] Shuai Tan,[1] Manh-Thuong Nguyen,[1] Grant E. Johnson,[1] Venkateshkumar Prabhakaran[1]

[1]Pacific Northwest National Laboratory

The extraction and separation of rare earth elements (REEs), particularly lanthanides, are critical for advancing technologies in renewable energy, electronics, and catalysis. However, their chemical similarity and comparable ionic radii make separating lanthanides challenging. Conventional REE separation technologies involving solvent extraction and ion exchange are energy intensive, pose environmental hazards, and involve toxic chemicals. Electrochemical separations, using redox-active electrodes, offer a sustainable and efficient alternative. Polyoxometalates (POMs), a class of multi-electron redox-active molecules, hold great promise for addressing these challenges in electrochemical separations. Their structural stability and capacity to selectively bind metal ions make POMs ideal candidates for the electrochemical separation of multicomponent REE mixtures. Therefore, understanding the POM-based redox electrode interface is critical for developing highly selective redox electrodes for lanthanide extraction. In this work, the Keggin-type tungsten POM was functionalized onto carbon nanotube surfaces using amine-based linkers to prepare a robust and selective redox interface for REE separations. The relationship between the charge state of the POM, coordination with targeted lanthanides (i.e., La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+}), and the effect of redox electron transfer kinetics was determined using operando electrochemical Raman spectroscopy combined with electrochemical impedance spectroscopy and *ab initio* molecular dynamics simulations. Our findings demonstrate the importance of understanding POM-based multielectron redox systems to overcome the challenges of electrochemical lanthanide separations, thereby paving the way for the development of advanced extraction methods for heavy-metal removal and critical mineral recovery.

Imaging ion transport and extraction of critical materials at the magneto-electrochemical separation interface

Ivani Jayalath,[1] Giovanna Ricchiuti,[1] Kevin Crampton,[1] Alan G. Joly,[1] Yang Huang,[1] Vignesh Sundaresan,[2] Venkateshkumar Prabhakaran[1]

[1]Pacific Northwest National Laboratory, [2]University of Mississippi, Oxford

Efficient separation of critical elements, including nickel (Ni), cobalt (Co), Neodymium (Nd), and dysprosium (Dy), is crucial for the development of advanced technologies like renewable energy systems, electric vehicles, and high-performance materials. Conventional techniques like solvent extraction and ion exchange, while widely used, are resource-intensive and environmentally unsustainable, underscoring the need for novel, sustainable separation strategies. Electrochemical separation is sustainable because of higher efficiency and ease of integration with available energy sources. Ion transport plays a pivotal role in controlling the efficiency and selectivity of electrochemical reactions at the electrode-electrolyte interface (EEI). Our research focused on leveraging external electric and magnetic fields to precisely control the selectivity of ion transport (transference number), heralding a shift in equilibrium ion concentration near the electrodes for selective electrodeposition or electrosorption of Ni^{2+}, Co^{2+}, Nd^{3+}, and Dy^{3+} in aqueous electrolytes.

Voltammetric techniques combined with x-ray photoelectron spectroscopy are used to reveal the selectivity of electrodeposition of Ni^{2+} and Co^{2+} with applied magnetic fields at EEI. In the case of Nd^{3+} and Dy^{3+}, voltammetric techniques combined with fluorescence and absorbance measurements are employed to determine the selectivity of ion enrichment at EEI. Advanced imaging techniques, including Scanning Electrochemical Cell Microscopy (SECCM) and Mach-Zehnder Interferometry (MZI), are employed to understand the interplay between concentration gradients, electric fields, and magnetic fields in driving selective ion separation. Overall, our research offers a sustainable and energy-efficient method for separating critical elements and establishes a pathway for designing next-generation separation systems for recycling battery materials and recovering rare earth elements.

Understanding magnetic-field-modulated dynamics and organizations of rare earth element ions at solid-liquid interfaces

Evan Angelo Mondarte,[1] Elias Nakouzi,[1] Jaehun Chun,[1] Venkateshkumar Prabhakaran,[1] Shuai Zhang[1]

[1]Pacific Northwest National Laboratory

External fields have been found to drive ion ordering and phase separation, which are useful for numerous applications such as microenvironment reactive chemistry, decontamination, and ion transport. Probing interfacial forces and high-resolution imaging are therefore vital in understanding this ion enrichment at interfaces. Through *in situ* high-resolution atomic force microscopy (AFM) and AFM-based force spectroscopy, we gained insights on the mechanism underlying the gathering and templating of rare earth elements (REE) ions at the solid-liquid interface in the presence of a magnetic field. Paramagnetic dysprosium (Dy^{3+}) ions undergo structuring on muscovite mica surface under a ~1500 G magnetic field. This ion structuring produces a repulsive force whose length and strength increase with rising ion concentration, occurring before a jump-to-contact regime toward a mica surface. Upon retraction from the mica surface, a strong adhesion force was observed, reminiscent of a bridging event between the tip and mica due to the high valency of the ion. In comparison, although the bridging force was also observed for diamagnetic lanthanum ions (La^{3+}), no concentration-dependent repulsive force prior to the jump-to-contact regime was observed. Preliminary results also indicate that the enrichment of Dy^{3+} ions at the surface generates a viscous layer. Overall, our non-invasive force mapping approach with high spatial and temporal resolution enables the study of non-equilibrium ion transport and nucleation driven by magnetic fields. This technique addresses challenges in critical material recovery by leveraging field-driven ion separations to enhance energy efficiency and selectivity while mitigating supply chain disruptions and environmental impacts.

Understanding ion dynamics at electrified interfaces during selective heavy metal recovery in ionic liquid-water electrolytes

Yang Huang,[1] Shuai Tan,[1] Manh-Thuong Nguyen,[1] Grant E. Johnson,[1] Venkateshkumar Prabhakaran[1]

[1]Pacific Northwest National Laboratory

The escalating environmental impact of heavy metal pollutants and the growing need for sustainable remediation techniques underscore the importance of improving recycling methods. Traditional chemical processes for recycling electronics are notably energy-intensive and unselective with the generation of hazardous waste. While electrochemical-based separation of rare earth elements (REEs) is more sustainable and energy efficient than traditional approaches, they currently face challenges in elemental selectivity due to the similarity in reduction potentials and other physicochemical properties of the REEs. This work focused on understanding the dynamics and reactivity of aqueous-mineral interfaces involving 1-ethyl-3-methylimidazolium chloride (C2mimCl) as a co-solvent ionic liquid (CSIL) with known amounts of lead and cadmium chloride ($PbCl_2$ and $CdCl_2$), two metals commonly used in batteries and found in contaminated environments. Our study explored the unique properties of CSILs at electrified interfaces that enhance elemental selectivity and recovery efficiency. We observed the interfacial structure and dynamics of C2mimCl and metal ions using several experimental techniques, including electrochemical impedance spectroscopy, Raman spectroscopy, and operando infrared spectroscopy, providing insights into the nucleation, growth, and dissolution processes occurring at the interface. Preliminary results indicate that specific interactions at the electrified interface facilitate the formation of a selective solvation shell, significantly enhancing the separation and recovery of Pb^{2+}. Our findings highlight the potential of using ionic liquids in engineered environments to improve the sustainability of heavy metal recovery processes. This effort contributes to reducing environmental contamination while extending the spatial and temporal characterization scales in interfacial science under complex environmental conditions.

Interfaces under complex and extreme environments: High salinity, pH, temperature, confinement, radiation and photocatalysis

Isotopic substitution provides mechanistic information on gibbsite dissolution in alkaline solutions representative of nuclear waste

Ashley Kennedy,[1] Emily Nienhuis,[1] Carolyn Pearce,[1] Trent Graham[1]

[1]Pacific Northwest National Laboratory

Plutonium production at the Hanford Site resulted in over 56 million gallons of nuclear waste, making it one of the most contaminated nuclear waste sites in the world. Hanford tank waste is characterized by extremes in alkalinity and low water activity, with chemical phenomena driven far from equilibrium by ionizing radiation. The Ion Dynamics in Radioactive Environments and Materials (IDREAM) Energy Frontier Research Center is researching knowledge gaps in these complex chemical environments. One of the primary chemical mysteries investigated by IDREAM is the solubility, nucleation, crystallization, and aggregation behavior of aluminum (oxy)hydroxides. Aluminum is a major component in the waste due to disposal of aluminum fuel cladding and the addition of aluminum nitrate as a “salting agent”. Aluminum crystallizes in an unpredictable manner from tetrahedrally coordinated aluminate anions in solution to octahedrally coordinated aluminum hydroxide polymorphs. Here, we investigate the role of hydrogen bonding and proton transfer by analyzing the kinetics of gibbsite ($Al(OH)_3$) dissolution and reprecipitation in sodium hydroxide or deuteroxide solutions over varying temperatures. Ultimately, IDREAM seeks to develop a mechanistic understanding of aluminum hydroxide crystallization in Hanford tank waste to accelerate ongoing retrieval and processing efforts.

Atomic-scale understanding of benzaldehyde hydrogenation mechanisms at Pd-water interfaces

Alexander von Rueden,[1] Julia B. Moreira,[1] Benjamin A. Jackson,[1] Thuy T. Le,[1] Udishnu Sanyal,[1] Simuck F. Yuk,[2] Mal-Soon Lee,[1] Johannes A. Lercher[1]

[1]Pacific Northwest National Laboratory, [2]United States Military Academy

Biomass is a promising alternative to crude oil as a carbon source for energy carriers and fine chemicals. Reduction of carbonyl groups within bio-oils, which are prone to polymerization, is necessary for increasing their stability. On this front, hydrogenation of benzaldehyde—the simplest aromatic aldehyde—can serve as an excellent model reaction. We have previously studied aqueous-phase (electro)catalytic benzaldehyde hydrogenation on Pt group metals, finding Pd to be both highly active and selective. Our current experimental efforts are aimed at elucidating the impacts of applied potential and H_2 pressure on the benzaldehyde hydrogenation mechanism over Pd, with both chemical and electrochemical steps being possible. To help answer these questions, we developed atomistic

models of adsorbed benzaldehyde at H-covered Pd-water interfaces under different electrochemical conditions. Using these models, we performed density functional theory (DFT)-based *ab initio* molecular dynamics (AIMD) simulations to probe the dynamic structures at the interface. We also used these structures as a starting point for reaction studies, in which we evaluated the different possible hydrogenation mechanisms. We reveal how different pH and surface charge conditions influence the dynamic structures of Pd-water interfaces. We also provide atomic-level mechanistic insights on benzaldehyde hydrogenation, complementing our experiments and offering a fundamental understanding that will help guide advancements in biomass upgrading.

Vibrational sum frequency generation spectroscopy at the nickel-iron alloy-electrolyte interface

Ezra Marker[1]

[1]Northwestern University

Vibrational sum frequency generation (SFG) spectra of the nickel-iron alloy:water interfaces at two potential conditions are presented (0.8 V vs 0.0 V). We find signatures of Stern layer water orientation depending on the potential. The results are discussed in the context of the nickel-iron alloy's non-resonant contribution to the SFG signal and water's own chi(3) contribution. Connections to molecular processes at the nickel-iron alloy surfaces relevant to electrochemistry are made.

Ni Impacts Yield and Products of Low-Water Carbonation of Forsterite (Mg_2SiO_4)

John S. Loring,[1] Bridgette N. Carven,[1] Zsombor Molnár,[1] Mark E. Bowden,[1] Sandra D. Taylor,[1] Libor Kovarik,[1] Christopher J. Thompson,[1] Kelly A. Peterson,[1] Zoltan Váci,[2] David A. Fike,[2] Young-Shin Jun,[2] Sebastien N. Kerisit[1]

[1]Pacific Northwest National Laboratory, [2]Washington University in St. Louis

Using carbon dioxide (CO_2) to recover nickel (Ni) by carbonating metal-silicate-rich (ultra)mafic ores can help the mining industry lower processing costs and reach net-zero CO_2 emissions. Furthermore, carbonation under low-water conditions could decrease water usage and minimize waste. In this study, we investigated the impact and fate of Ni during carbonation of Ni-doped forsterite (Mg_2SiO_4) in CO_2 at 50 °C and 20 bar for 12 days at both 85% and 96% relative humidity (RH). Total carbon analysis indicated that higher RH led to greater reactivity. However, 5% Ni-doping reduced the extents of reaction by approximately half compared to carbonation of pure forsterite under identical conditions, likely due to a combination of kinetic and thermodynamic factors. X-ray diffraction, infrared spectroscopy, and scanning electron microscopy showed that the carbonation of Ni-doped forsterite produced exclusively magnesite ($MgCO_3$), while both magnesite and hydromagnesite precipitated during the carbonation of pure forsterite. Small-angle X-ray scattering showed that carbonated pure and Ni-doped forsterites were covered in 1–1.5-nm layers of amorphous silica (SiO_2(am)), but transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDS) indicated that SiO_2(am) was also present in patches, more so for pure forsterite and for samples reacted at higher RH. TEM-EDS analysis of a cross section of a magnesite particle precipitated during the carbonation of a 2% Ni-doped forsterite indicated that Ni was homogenously distributed within the particle. This fundamental knowledge will enable predictions of conditions conducive to employing low-water carbonation to recover Ni from (ultra)mafic ores.

Influence of anions on electrical double layer structure at charged silica interfaces under varying pH

Preeti Gahtori,[1] Paul Elinkpo,[1] Julianne M. Gibbs[1]

[1]University of Alberta

The interfacial structure of the electrical double layer (EDL) at charged solid-liquid interfaces has been extensively studied, with significant focus on counterion effects under various conditions. However, the role of co-ions, particularly under varying pH conditions, remains less explored. In this study, we investigate the surface charge density at the shear plane and compare it with the total surface charge density. Using zeta potential measurements and potentiometric titrations, we examine the behavior of different anions (ClO_4^-, Cl^-, and SO_4^{2-}) with Na^+ counterions on planar silica surfaces and colloidal silica across a wide pH range. Our findings reveal that anions, often presumed to be repelled at basic pH, exhibit distinct surface interactions depending upon the pH. At moderately basic pH (8–9.5), perchlorate and chloride ions provide evidence of adsorption at the silica surface, while sulfate ions, due to their higher hydration, are primarily repelled. However, at higher basic pH (9.5–11.5), sulfate ions show substantial increase in the magnitude of the surface charge density at the shear plane relative to Cl^- and ClO_4^-. This is likely due to ion pair formation in sodium sulphate, which suppresses the release of Na^+ to the negatively charge silica. At acidic pH, surface charge density magnitude decreases for all anions due to the reduction in negatively charged silica sites, except for NaCl, where chloride ion increases the negative zeta potential suggesting overcharging. These findings highlight the complex interplay of ion-specific effects and pH-dependent behavior of EDL, providing new insights into ion distribution and surface charge dynamics.

Theories for interface structure, dynamics, and charge transfer

Multiscale computational modeling of the interface and evaporation in acetonitrile-water-amino acid droplets for electrospray ionization

Samantha Johnson,[1] Swarup Banerjee,[1] Wilma Rishko,[2] Marcel Baer,[2] Simone Raugei[2]

[1]Colorado School of Mines, [2]Pacific Northwest National Laboratory

Identifying molecules and elucidating their chemical structure are ubiquitous problems in chemistry. Mass spectrometry (MS) has been applied for these purposes due to its versatility, as it can be applied to single compounds or complex mixtures. However, MS is sensitive to the parent medium (matrix effects) and instrument conditions, making unambiguous identification and quantification difficult. We develop continuum-scale and atomistic computational approaches to understand how the reactive environment in droplets created during soft ionization processes such as electrospray ionization affect mass spectra, particularly in mixed solvent systems. Chemical transformations can still occur in the microsolvated phase between condensed and gas phases, and may even be accelerated. However, the breadth of time and length scales make electrospray difficult to model with a single computational approach. Thus, we use a combination of classical molecular dynamics and density functional theory energy calculations. For nanometer-sized droplets, we use molecular dynamics to probe kinetics of droplet interface formation. Using experimentally relevant concentrations of analyte and solvents, we show that systems with mixtures of acetonitrile, water, and amino acids lead to the enrichment of

acetonitrile and amino acids at the droplet's surface. From these simulations, information about the heterogeneous environment around amino acids is gleaned, leading to better understanding of the reactive environment. We then investigate the kinetics of droplet evaporation to show that while the evaporation rate of the droplets is sensitive to concentration and droplet size, the barriers for evaporation of water vs acetonitrile in mixed droplets are similar due to reduced hydrogen bonding.

Interactions of polar and non-polar groups of alcohols in zeolite pores

Benjamin Jackson,[1] Ruixue Zhao,[2] Sungmin Kim,[1] Mal-Soon Lee,[1] Fuli Deng,[1] Xiaomai Chen,[2] Konstantin Khivantsev,[2] Yue Liu,[2] Vassiliki-Alexandra Glezakou,[1] Roger Reusseau,[1] Johannes A. Lercher[1]

[1]Pacific Northwest National Laboratory, [2]Technical University of Munich

Zeolites are tectosilicate which are frequently used as industrial catalysts and sorbents with applications of dehydration, cracking, dehydrogenation, isomerization, and alkylation. Given this, an explicit understanding of the interactions of zeolite pores and acid-base sites with sorbates is critical for efficient reaction design. Zeolite pores consist of tetrahedral silica walls, generally considered “hydrophobic”, while substituted acid-base sites, such as bridging Si-OH-Al, are considered “hydrophilic.” Interactions of non-polar molecules in these pores rely predominantly on dispersion forces influenced by the molecule size, zeolite channel size and pore structure while sorption of polar molecules like water is dictated through electrostatic or hydrogen bonding interactions. Here, C1-C4 primary alcohols are utilized to provide a discrete description of the interplay between non-polar and polar interactions within zeolites MFI and Beta. Three types of interactions were identified, i.e., the interaction of CHx groups of the alkyl chain with the zeolite pore walls (~10 $\text{kJ}\cdot\text{mol}^{-1}$ per carbon), the interaction of the alcohol hydroxyl group with the pore walls (30–35 $\text{kJ}\cdot\text{mol}^{-1}$), and the interaction of the alcohol hydroxyl group with Brønsted acid sites (BAS, 37 $\text{kJ}\cdot\text{mol}^{-1}$). A combined approach utilizing experimental calorimetry and computational modeling is used to provide insights critical to the design of catalysts with tailored catalytic activity and selectivity.

Interface investigation of *de novo* allosteric two-component protein tubes on mineral surfaces

Chenyang Shi,[1] James De Yoreo[1]

[1]Pacific Northwest National Laboratory

The behavior of proteins at solid-liquid interfaces is pivotal for advancing human-machine interfaces and biomedical technologies. Despite their distinct biological activities and functionalities, the mechanisms underlying protein interfacial behavior remain poorly understood. Morphological adaptations driven by secondary structural changes further enhance the complexity and dynamism of these systems. Maintaining structural uniformity within a protein’s internal configuration while permitting external morphological diversity offers a promising strategy to elucidate interfacial behavior.

In this work, we utilized *de novo* proteins that form tubular architectures through hydrophobic interactions between two distinct components. These proteins exhibit diverse morphologies, including small tubes (S), large tubes (L), and helical tubes (H), with unique energy landscapes in aqueous environments. While L and H tubes exhibit higher energy barriers compared to S tubes, they eventually dominate during temporal evolution. Notably, the deposition and orientation of these tubular structures on mineral surfaces are strongly influenced by local salt ion concentrations, which are modulated by the mineral interface's structural properties. Interaction strength increases significantly at potassium ion concentrations of 1–3 M, driving ordered deposition. S tubes align precisely with the mineral surface lattice, whereas L and H tubes exhibit fluctuations between low energy orientations within their angle-dependent energy landscapes. This work underscores the intricate interplay between protein structure, environmental factors, and interfacial behavior, providing new insights into protein interactions at solid-liquid interfaces.

Mechanisms of lanthanum precipitation on gibbsite surfaces: Insights from AFM and 3D fast force mapping

Shuhong Song[1]

[1]Pacific Northwest National Laboratory

The precipitation of rare earth elements (REEs) on common alumina and aluminosilicate minerals has recently attracted significant attention, due to the need to secure domestic supply chains for these critical elements. REE precipitation is driven by subtle and poorly understood interactions between surface charging, ion correlations, solution structure, surface tension, and epitaxial strain. Depending on the solution saturation, carbonate saturation, and pH, varied phases may also be obtained, ranging from hydrated to carbonate phases such as $La_2CO_3{\cdot}8H_2O$ to hydroxides such as $La(OH)_3$. Advances in atomic force microscopy (AFM) and AFM-based three-dimensional fast force mapping (3D FFM) techniques have enabled a detailed exploration of the fundamental mechanisms underlying REE precipitation. In this study, we focus on the precipitation of lanthanum on gibbsite surfaces. Using AFM, we observed the adsorption of La^{3+} ions and precipitation of different lanthanum phases at varying La^{3+} concentrations and pH levels. We see signs of ion adsorption and preferential associations with surface topography such as steps and terraces prior to precipitate formation. To further reveal the precipitation mechanisms, we compared charge distributions and solution structures above the gibbsite surface both in the absence and presence of lanthanum using 3D FFM. This comparison provides new insights into the association of REE ions with key mineral surfaces, and reveals the impacts of surface defects and the local electrostatic environments. Our findings contribute to a better understanding of REE geochemistry, which is critical for diversifying REE sources, and provide a foundation for future studies on interfacial precipitation mechanisms.

Tuesday, May 20, 2025 – Abstracts

Topic A: Frontiers in computation and advances in analytical techniques

Tuesday, May 20th, 2025, 9:00 AM – 11:35 AM PST

Discovery Hall A/B/C

Discussion Leaders: Franz Geiger (Northwestern University), Eric Borguet (Temple)

9:05 AM – 9:50 AM Keynote

A molecular view of water interfaces

Mischa Bonn[1]

[1]Max Planck Institute for Polymer Research

Water interfaces differ from the bulk, in both their physical structure and chemical composition. In particular, the role of the termination of the hydrogen-bonded network, the role of charges at interfaces, and the effect of charges on the arrangement of counterions and water have been much debated. These charges also affect the chemical dynamics occurring at water interfaces. For instance, charge is relevant for "on-water chemistry" – chemistry at the open water surface, relevant for both technologies and chemical processes in the atmosphere.

My presentation will show how we can characterize the outermost monolayer of water at an interface, using advanced, femtosecond laser-based techniques. These techniques allow to quantify the interfacial ion distribution, and follow chemical conversion at water surfaces and interfaces in great detail using surface-specific vibrational spectroscopies.

10:05 AM – 10:35 AM Invited

Can we exploit hydrophobicity to regulate the chemistry at electrified metal-water interfaces?

Simone Pezzoti[1]

[1]ENS, CNRS

Adsorption of ions and hydrophobic solutes are key processes in electrochemistry. The former regulates the Electric Double Layer and dictates important quantities, e.g., capacitance. The latter has major implications for heterogeneous catalysis, where small hydrophobic molecules are commonly involved as reactants and products. Despite solvation of charged and hydrophobic species are remarkably different, I will show in this presentation that the exotic way hydrophobicity arises at electrified metal-water interfaces influences both of them with a common underlying molecular mechanism.[1-3] I will first show from classical molecular dynamics[1] that the peculiar molecular arrangement of

electrified gold/water interfaces induces atypical fluctuations of the liquid water density, resulting in a hydrophobic water-water interface formed close to the metal. I will then illustrate how such hydrophobicity dictates solvation free energy and regulates the accumulation of hydrophobic solutes (e.g., CO),[1,3] as well as some ions (e.g., Cl^-),[2] at the interface. I will finally discuss some implication of these findings for electrochemical reactions, with examples for CO^+ and N_2 reduction, as well as acid-base chemistry.[1,5] I will finally extend toward oxide-water interfaces and chemistry therein.

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10:35 AM – 11:05 AM Invited

Phase-resolved nonlinear spectroscopy of mineral/water interfaces

Satoshi Nihonyanagi[1]

[1]RIKEN

Vibrational sum frequency generation (VSFG) is a powerful technique for studying the structure and orientation of molecules at interfaces, owing to its intrinsic interface selectivity based on second-order nonlinear optics. Furthermore, the phase-resolved version of VSFG technique, Heterodyne-detected VSFG (HD-VSFG) spectroscopy enables us to obtain real (Re) and imaginary (Im) parts of the second-order nonlinear susceptibility (X(2)) spectrum separately. The sign of an ImX(2) spectrum provides decisive information about the up/down orientation of interfacial molecules, which is a unique advantage of HD-VSFG spectroscopy. In the past decade, HD-VSFG has been extensively used for investigating various aqueous interfaces.

In this talk, I will focus on oxide/water interfaces, namely, silica/water and alumina/water interfaces. These interfaces are ubiquitous on Earth and are prototypical negatively and positively charged mineral interfaces. We have measured ImX(2) spectra of silica/water and alumina/water interfaces with various salt concentrations at a wide range of solution pHs. Analysis of the salt dependence of the ImX(2) spectra enabled us to separate the spectral components of the topmost interfacial water from that in the diffuse electric double layer (DL). It was found that the ImX(2) spectra of water at the silica interface exhibit a characteristic interface-specific spectral component, whereas, that at the alumina interface exhibit no such characteristic component, indicating a strong interaction at the silica surface and no/weak interaction at the alumina interface. Moreover, ImX(2) spectral components of water in DL of both interfaces can be described well by the Modified Gouy-Chapman theory, providing good models of charged mineral/water interfaces.

11:05 AM – 11:35 AM Invited

Advances in simulating redox dynamics at iron oxide/water interfaces with reactive neural network potentials

Kevin Rosso,[1] Kit Joll,[2] Philipp Schienbein,[2] Jochen Blumberger[2]

[1]Pacific Northwest National Laboratory, [2]University College of London

Mechanisms of autocatalytic redox reactions between aqueous Fe(II) and Fe(III)-oxides have long been challenging to unravel due to the coupling of valence interchange electron transfer, hydrolysis, and proton transfer at the interface. Iron oxides are wide band gap semiconductors with a narrow conduction band arising from strongly localized 3d orbitals. Consequently, charge carriers tend to self-trap as polarons whose mobilities are controlled by thermally activated site-to-site hopping. Theories implemented in various modern day computational chemistry tools encompass all these system characteristics but their simultaneous description within a single framework remains out of reach. To this end, we present a reactive neural network potential-based molecular dynamics approach to simulate the initial interaction of aqueous Fe(II) hexaquo cations on the (001) surface of hematite. Prior to treatment of electron exchange, the method must prove capable of accurately describing the ligand and proton exchange processes that enable Fe(II) adsorption to the surface. Using *ab initio* molecular dynamics simulations for isolated iron aquo cations and also for hematite-water interfaces as training data sets, we developed a single neural network potential of the Behler-Parrinello type that can accurately predict solvation structure and rate constants for water exchange for aqueous Fe(II), the surface structure of hematite (001) in water, and the formation of stable Fe(II) surface complexes. The neural network potential developed herein allows one to converge free energy profiles and transmission coefficients at density functional theory-level accuracy, outperforming state-of-the-art classical force field potentials. With further development, machine learning potential molecular dynamics should be able to describe the electron exchange process at the interface. This simulation approach may thus ultimately enable the first comprehensive insights into the complex multi-step processes that give rise to nanoscale experimental observables such redox-catalyzed dissolution or growth at this interface.

Topic A: Frontiers in computation and advances in analytical techniques

Tuesday, May 20th, 2025, 1:20 PM – 5:10 PM PST

Discovery Hall A/B/C

Discussion Leaders: James Kubicki (University of Texas El Paso), Maria Susko (Pacific Northwest National Laboratory)

1:30 PM – 2:00 PM Invited

Understanding the OER mechanism on hematite photoanodes through nonlinear optical spectroscopy and photocurrent kinetics

R. Kramer Campen,[1] Yuke Yang,[1] Yujin Tong[1]

[1]University of Duisburg-Essen

Hematite is an attractive photoanode for the oxygen evolution reaction (OER). However, insight into reaction mechanism, and thus the capability to rationally optimize performance, is limited by the challenge in relating band bending, surface state population and chemical reactivity. Conventionally the first two issues are addressed by electrochemical impedance spectroscopy (EIS) and photocurrent/voltage measurements while the later is addressed indirectly -- through measurement of reaction rate as a function of overpotential or current/voltage transients -- or through operando characterization of the electrode/electrolyte interface using bulk sensitive spectroscopies. Unambiguous interpretation of all of these types of measurements is challenging. Ideally we'd like a single technique that offers the possibility of directly characterizing both the extent of band bending and surface chemical speciation under operando conditions.

Vibrational Sum Frequency Generation (VSFG) spectroscopy, is interface-specific by its symmetry selection rules and sensitive to interfacial electric fields. Here I describe our recent efforts using VSFG to probe the development of photovoltage and the steady-state population of possible intermediates in the OER at the pulsed laser deposited (PLD) hematite/alkaline electrolyte interface operando. By concurrently performing VSFG and conventional electrochemical characterization we unambiguously relate the potential dependence of photovoltage, the onset of the OER and the attendant change in surface chemical speciation. Our steady-state experimental observables can be quantitatively reproduced by a model of model of OER kinetics on Hematite via a single-hole mechanism and are consistent with ultrafast dynamics we observe in the same system in optical pump - VSFG probe experiments.

2:00 PM – 2:15 PM

Bridging electrochemistry and nonlinear optics: Studying the oxygen evolution reaction using second harmonic generation

Raiden Speelman,[1] Franz Geiger[1]

[1]Northwestern University

With the push for more renewable energy sources, understanding the chemical reactions that drive their production is crucial. Many key reactions leading us toward a greener future are powered by electrochemistry. One particularly important electrocatalytic reaction is the oxygen evolution reaction (OER). In solar fuel cells, the OER is typically paired with the hydrogen evolution reaction (HER) to provide a renewable alternative in the form of hydrogen fuel. However, solar fuel cells face challenges because the most efficient electrocatalysts are expensive platinum group elements, while earth-abundant catalysts exhibit large overpotentials. To improve the viability of these earth-abundant catalysts, it is vital to investigate the causes of the overpotential. Unfortunately, many techniques used to study electrocatalytic reactions encounter difficulties when applied *in situ* and operando. To advance our understanding of these critical reactions, it is essential to conduct studies under working conditions. We are developing surface-specific spectroscopic techniques to bridge the gap between electrochemical reactions and spectroscopy, thereby enhancing our insight into these complex mechanisms. These techniques include phase-resolved second harmonic generation, sum frequency generation, and resonantly-enhanced second harmonic generation.

2:15 PM – 2:30 PM

Continuum embedding for all-electron density functional theory simulations of electrochemical interfaces

Jakob Filser,[1] Edan Bainglass,[2] Karsetn Reuter,[3] Oliviero Andreussi[1]

[1] Boise State University, [2] Paul Scherrer Institute, [3] Fritz Haber Institute of the Max Planck Society

Recent advances in continuum embedding models have enabled the incorporation of solvent and electrolyte effects into density functional theory (DFT) simulations of materials surfaces, significantly benefiting studies of electrochemistry, catalysis, and other energy-related applications. By representing solvents and electrolytes as structureless continuum media, these models dramatically reduce computational costs compared to the thermodynamic sampling of liquids with atomistic details, thereby enabling large-scale and high-throughput computational investigations. To extend the simulation of diverse systems and properties, the implementation of continuum embedding models into the Environ library adopts a modular programming paradigm, offering a flexible interface for communication with various DFT programs. The speed and scalability of the current implementation rely on a smooth definition of the key physical properties of the atomistic system, in particular of its electronic density. This has hindered the coupling of Environ with all-electron simulation packages, as the sharp electron density peaks near atomic nuclei are difficult to represent on regular grids. In this work, we introduce a novel smoothing scheme that transforms atom-centered electron densities into a regular grid representation while preserving the accuracy of electrostatic calculations. This approach enables a minimal and generic interface, facilitating seamless interoperability between Environ and all-electron DFT programs. We demonstrate this development through the coupling of Environ with the FHI-aims package and present benchmark simulations that validate the proposed method. This advancement opens the door to capturing explicit core states and derived properties at wet electrified interfaces, with direct relevance to energy storage and conversion devices.

2:50 PM – 3:20 PM Invited

Determining the dielectric constant of solid/liquid interfaces

Eric Borguet[1]

[1]Temple University

The dielectric constant (ε') of interfacial water is an important parameter, but its measurement has posed challenges, and no consensus has been reached on a generalized expression. We derived a formula for ε' of a buried interface using the slab model for a half-solvated sphere and show that this analytical expression, based on classical continuum electrostatics, agrees well with values for the interfacial dielectric constant based on Molecular Dynamics simulations.[1] We experimentally validated this expression using vibrational sum frequency generation and Fresnel factor calculations for interfaces of alumina with water (H_2O and D_2O) as well as acetonitrile/Al_2O_3 interfaces. We discuss the impact of the observed reduction in the interfacial dielectric constant, compared to the bulk liquid value, on interfacial phenomena ranging from ion pairing to vibrational energy relaxation. This fills an important knowledge gap in the description of the dielectric constant of interfaces.

1. Determining the Dielectric Constant of Solid/Liquid Interfaces, Somaiyeh Dadashi, Narendra M. Adhikari, Hao Li, Stefan M. Piontek, Zheming Wang, Kevin M. Rosso, and Eric Borguet (submitted)"

3:20 PM – 3:35 PM

Temperature dependent proton coverage and total potential at fused silica-water interfaces from phase-resolved nonlinear optics

Nicole Gonzalez,[1] Amani Alghamdi,[1] Franz Geiger[1]

[1]Northwestern University

We present a blueprint for second harmonic generation (SHG) amplitude and phase measurements at buried aqueous interfaces using an affordable Y-crystal based oscillator. A Galilean beam expander addresses the signal vs. local oscillator mismatch, while a beam block eliminates otherwise interfering front reflections from the flat optical windows used here. The instrument is applied to study the temperature dependence of interfacial amphoterism via phase- and amplitude-resolved SHG measurements at the fused silica:water interface, providing total interfacial potential estimates from 20°C to 60°C. Results show nearly linear voltage increases with temperature that rise faster at low vs. high ionic strength and are consistent with temperature-dependent equilibrium constants governing the amphoteric silica:water interface. Proton surface coverages at pH 2.5, 5, and 11 increase with temperature as the surface becomes more negatively charged, reaching up to 10^{13} protons cm^{-2} at

60°C. These findings aid interfacial model development, benchmark atomistic simulations, explore temperature-dependent Hofmeister effects, and enhance understanding of interfacial electrocatalysis.

3:35 PM – 3:50 PM

Interfacial quantum electric fields

Shawn Kathmann, Michael LaCount,[1] Sten Lambeets,[1] Daniel Perea,[1] Tanya Prozorov[2]

[1]Pacific Northwest National Laboratory, [2]Ames National Laboratory

Electric fields and voltages within and at the interfaces of matter are relevant to catalysis, crystallization, materials science, biology, and aqueous chemistry. Accurate measurements of fields and voltages of matter has been achieved using electron holography/tomography (EHT) and can be directly compared with quantum mechanical calculations. From these findings all interfaces have large intrinsic local electric fields (~10 GV/m = 1 V/Å) and voltages even if these materials are macroscopically electrically neutral. The use of very weak applied fields ($<10^{-3}$ V/Å) causes materials to respond, changing both the magnitude and spatial distribution of the intrinsic electric fields. The resulting interfacial response fields, i.e., Eresp(r) = Eintr(r) + Eappl(r), have been measured using EHT and are similarly large as the intrinsic fields even though the applied field is very weak. These large fields can and do alter adsorbed species electronic states (e.g., bonding/antibonding orbitals, luminescence, chemical reaction barriers, electron transfer, etc.) as well as rotational and vibrational states. When characterizing fields and voltages in matter, it is essential to specify exactly where they are being evaluated and over what spatial regions of the quantum charge density do different measurements probe (e.g., electron holography tomography vs. vibrational Stark spectroscopies). Here we outline the chemical physics, quantum, and statistical mechanics relevant to these findings and their consequences on how we understand, control, and exploit interfacial fields.

4:10 PM – 4:40 PM Invited

Advancing energy and environmental technologies through high-accuracy simulations

Hendrik Heinz,[1] Cheng Zhu,[2] Krishan Kanhaiya,[3] Shiyi Wang,[4] Jordan Winetrout[1]

[1]University of Colorado Boulder, [2] Guangdon Israel-Technion,[3] University of Bochum,

[4] Lawrence Berkeley National Laboratory

The simulation of metals, oxides, and solid-electrolyte interfaces is essential for advancing energy technologies such as fuel cell catalysts, water splitting, hydrogen storage, bioinspired materials, and geochemistry applications. Computational and AI-driven methods accelerate progress but often lack accuracy, especially when relying on DFT or DFT-derived approaches.

This work highlights molecular dynamics (MD) simulations with beyond-DFT accuracy using the INTERFACE force field (IFF) and reactive INTERFACE force field (IFF-R). Achieving up to 0.1 kcal/mol (0.004 eV) precision, critical for catalytic systems, these models outperform standard DFT and DFT/ML methods. Key examples include:

1. Platinum catalysts for oxygen reduction reaction (ORR): A 0.6 kcal/mol (0.025 eV) difference doubles catalytic activity.

2. Peptide binding to MoS_2: Insights into molecular interactions and assembly.

3. Water layering and organic molecule assembly on surfaces: High-resolution interfacial phenomena.

IFF and IFF-R offer up to 10× higher accuracy than DFT/ML and 100× compared to earlier force fields, with faster performance and superior interpretability. Their seamless compatibility across material types and integration with established parameter sets (CHARMM, AMBER, etc.) ensure broad applicability. Recent advances include bond formation/breaking simulations to predict mechanical properties and potential automation via AI-driven approaches.

References: (1) doi:10.1021/acs.jctc.3c00750 (2023). (2) doi:10.1021/acsnano.2c10953 (2023). (3) doi:10.1126/sciadv.ado3942 (2024). (4) doi:10.1038/s41929-024-01175-8 (2024). (5) doi:10.1021/acs.jctc.0c01132 (2021).

4:40 PM – 4:55 PM

Rapid screening of single atom catalyst synthesis conditions using ToF-SIMS and facet-dependent single-crystal substrates

Juejing Liu,[1] Ping Chen,[1] Yadong Zhou,[1] Zheming Wang,[1] Carolyn Pearce,[1] Kevin Rosso,[1] Xin Zhang[1]

[1]Pacific Northwest National Laboratory

Single-atom catalysts (SACs) offer superior catalytic performance compared to traditional nanoparticle catalysts but are challenging to develop because of the need for extensive optimization and specialized characterization techniques. This study presents a rapid and versatile method for detecting synthesis conditions and elucidating deposition mechanisms of SACs on various substrates. By depositing active elements (Au, Cu, Ni and Rh) on facet-specific single-crystalline substrates (CeO_2, TiO_2, MgO and Al_2O_3) and employing time-of-flight secondary ion mass spectroscopy (ToF-SIMS), we assessed facet-dependent deposition behaviors and identified optimal conditions for solution-based SAC synthesis. On CeO_2 and TiO_2, we confirmed facet-dependent deposition, primarily influenced by oxygen vacancy density and photocatalytic activity, respectively. MgO exhibited the formation of metal oxide/hydroxide clusters for all active elements, and the degree of clustering for Cu and Ni was correlated with the facet hydrolysis susceptibility. Notably, Au and Rh deposition on MgO was facet-independent, attributed to the formation of hydroxide species in solution. Al_2O_3, due to its chemical stability and lack of surface defects, did not show active element deposition. This study not only provides a time and cost-efficient method for prescreening SAC synthesis conditions, but it also provides valuable insights into the various deposition mechanisms governing SAC formation on different substrates, paving the way for the rational design of tailored SACs for various catalytic applications.

4:55 PM – 5:10 PM

N_2 electro-activation over Ru using *operando* atom probe microscopy

Sten Lambeets,[1] Mark Wirth,[1] Daniel E. Perea,[1] Shawn Kathmann[1]

[1] Pacific Northwest National Laboratory

The growing demand for green electricity and energy storage solutions has created interest in ammonia (NH_3) as a potential low-carbon fuel storage solution. The electrochemical nitrogen reduction reaction (NRR) to synthesize NH_3 is a key process under extensive investigation, with single-atom electrocatalysts (SACs) demonstrating promising potential. Due to their unique morphology, SACs experience localized intense external electric fields (EFs) when subjected to an applied potential. While theoretical studies highlight the transformative impact of EFs on SAC performance, the precise field strengths and underlying mechanisms remain largely unexplored.

Atom Probe Microscopy (APM) techniques, including Field Ion Microscopy (FIM) and Operando Atom Probe (OAP), are uniquely suited to investigate these mechanisms at the nanoscale, as their imaging inherently relies on EFs. This investigation combines these capabilities to examine nitrogen (N_2) dissociation adsorption on ruthenium (Ru) surfaces at room-temperature. Under controlled conditions—EFs of ~13–15 V/nm, a temperature of 300 K, and a N_2 pressure of 1.4×10^{-7} mbar—the field either ionizes N_2 molecules directly or enhances their dissociation.

Results reveal that dissociated nitrogen (N(ads)) predominantly adsorbs on Ru{10-12} and Ru{21-14} facets. These findings underscore the intricate relationship between local surface structures, HEEFs, and catalytic behavior, offering new insights into the role of electric fields in the NRR and advancing the development of NH_3 as a sustainable energy carrier.

Topic B: Emerging applications and tools for energy challenges

Emerging applications and tools for energy challenges

Tuesday, May 20th, 2025, 1:20 PM – 5:10 PM PST

Discovery Hall D/E

Discussion Leaders: Kevin Leung (Sandia National Laboratories), Zheming Wang (Pacific Northwest National Laboratory)

1:30 PM – 2:00 PM Invited

Unraveling Cross-Cutting Mechanisms at Aqueous Interfaces: Advancing Predictive Models for Environmental and Technological Materials

Sara E. Mason[1]

[1]Brookhaven National Laboratory

Interfacial processes in aqueous environments are central to both environmental and technological challenges, requiring robust methodologies to capture complex behaviors across diverse materials. This talk highlights an integrated theoretical and computational framework that combines density functional theory (DFT), thermodynamic modeling, and electrochemical principles to elucidate mechanisms at mineral-water and advanced material interfaces.

Case studies on hematite (α-Fe_2O_3) and alumina (α-Al_2O_3) demonstrate how molecular-level insights into contaminant binding—such as oxyanions, heavy metals, and organic species—translate to predictive adsorption energetics. These findings emphasize the influence of surface composition and subtle adsorption-induced relaxations on environmental processes. Parallel investigations into complex metal oxides, including $Li(Ni_xMn_yCo_{1-y-x})O_2$ cathodes for lithium-ion batteries, uncover compositional design principles to optimize performance while mitigating sustainability concerns. Integrating these models with experimental efforts provides key descriptors for understanding metal release profiles, informing the design of environmentally safer nanomaterials.

Building on these foundations, we incorporate stochastic and machine-learning-driven approaches to explore non-intuitive interfacial structures and property-descriptor relationships, extending our understanding to emerging materials like MXenes and those used in nano-enabled agriculture. Collaboration with experimentalists ensures the methodology bridges fundamental surface science with real-world applications, enabling discoveries that address critical challenges in catalysis, energy storage, water purification, and environmental remediation.

2:00 PM – 2:15 PM

A generalized AI tool set for spectroscopy analysis: Examples on UV-VIS, Raman, and Fluorescence

Chris Young[1]

[1]Pacific Northwest National Laboratory

Despite rapid technological developments, analyzing spectra from UV-Vis, Raman, XRF, fluorescence, etc. remains a largely subjective and time-consuming task. The recent advancements in high throughput data collection creates further challenges to manual data analysis. While machine learning-based analysis was enabled for certain techniques, such as Raman and NMR, a universal, automatic, and high throughput spectrum analysis has not yet been developed. Here in, we propose an end-to-end automatic analysis pipeline utilizing four specialized convolutional neural networks (CNNs) that process raw spectra realizing de-noising, background removal, peak detection, and peak intensity and FWMH retrieval. For de-noising, a hierarchical UNET architecture outputs smoothed spectra with a mean squared error below 2.26×10^{-4} %. Our approach introduces a pyramidal UNET architecture for baseline removal, achieving a mean squared error below 6.38×10^{-4} %. For peak detection, we develop a deep-cascading UNET-hybrid architecture coupled with our inhouse loss function, demonstrating 94.1% accuracy compared to 81.7% with traditional cross-entropy and mean square error loss approaches. A similar architecture, when trained with additional peak location data, achieves human-expert level accuracy in peak intensity and FWMH determination on experimental data. Our automated pipeline significantly improves the efficiency and objectiveness of spectroscopy data processing by minimizing the human intervention, eventually contributing to high throughput data analysis and large-scale spectroscopy dataset construction.

2:15PM – 2:30PM

An Introduction to Neutron Reflectometry and the specific case of Atmospheric Aerosol Oxidation

Rebecca Anderson[1]

[1]Oak Ridge National Laboratory

Neutron reflectometry is a powerful tool for probing the composition of materials at buried interfaces, such as the mineral-aqueous interface. It provides sub-nanometer resolution of structure perpendicular to the interface and has good sensitivity to lighter elements, as well as some isotopic variation. The ability of neutrons to penetrate through sample environment chambers also allows for in-situ or operando measurements under a variety of conditions, such as changes in flow, confinement, temperature, pressure, humidity, and pH. This technique has been applied to a wide range of questions across energy and environmental themes including energy storage, catalysis, water purification, atmospheric chemistry, lubrication, and oil-recovery.

This presentation will introduce neutron reflectometry with highlights of its capability and limitations in energy and environment research, followed by a specific example focusing on the oxidation of atmospheric aerosol.

Atmospheric aerosols are important to the Earth’s climate, impacting the degree of light scattering (albedo) and precipitation. These aerosol particles can accumulate organic thin films from various natural and anthropogenic sources, which have been shown to affect the aerosol’s stability and light scattering properties. However, these films are typically not included in climate models. Coupled to this, the atmosphere is highly oxidizing which means these films can react during the aerosol’s lifetime altering this climatic influence. Using neutron reflectometry, we have measured the oxidation reaction rates of these organic films in the presence of different oxidants, extracting parameters to feed into climate models to improve our understanding of their climatic importance.

2:50PM – 3:20PM Invited

Birnessite-Tl(I) oxidative and non-oxidative interaction pathways. Can birnessite oxidize water?

Mario Villalobos,[1] Rodrigo J. Martínez,[1] Mismel Ruiz-García,[2] Yusniel Cruz-Hernández[3]

[1]Universidad Nacional Autónoma de México, [2]Advanced Environmental Laboratories, [3]Malvern Panalytical

Hexagonal poorly crystalline birnessite is a very abundant Mn oxide mineral. It shows a high reactivity that stems from its various structural properties: its very small particle sizes yield a considerable surface reactivity, but also, its large contents of cationic vacant sites inside the laminar structure drives a distinctive internal affinity towards cation binding. In addition, it has a very high oxidative capacity towards redox-sensitive species. In the present work we will show that the interaction of birnessites with thallium (I) includes all of the above possibilities, depending on the mode and dose of Tl(I)/Mn additions. In birnesssite oxidative interactions there is naturally Mn reduction, therefore it is important to not just follow the transformation of the interacting species, but also the resulting structures from the reacting solid. We will show that upon reaction with Tl(I), birnessite may oxidize a large fraction of it to Tl(III) and partially dissolve, increasing its solid-Mn(III) content. But it also may trigger birnessite to oxidize water, instead of Tl(I), and produce oxygen, and concurrently the layered structure of the mineral transforms to a 2x2 tunneled cryptomelane-like structure, where the tunnel centers are occupied by non-oxidized Tl+. Although we do not know yet the specific factors that explain the different reaction pathways, we found the Tl(I)/Mn ratio and mode of addition to be the key conditions for defining these pathways. We used powder X-ray Diffraction, X-ray Absorption Spectroscopy, Density Functional Theory, along with wet chemical methods of sorption isotherms and an oxygen generation probe.

3:20PM – 3:35PM

Tuning the structural and electronic properties of high entropy oxide thin films for water oxidation

Le Wang,[1] Krishna Prasad Koirala,[1] Minju Choi,[1] Anton Tadich,[2] Dongchen Qi,[3] Mark Bowden,[1] Hsin-mei Kao,[1] Zihua Zhu,[1] Yingge Du[1]

[1]Pacific Northwest National Laboratory, [2]Australian Synchrotron, [3]Queensland University of Technology

High-entropy perovskite oxides extend the versatility of conventional $AB0_3$-type perovskite oxides by incorporating multiple equiatomic A-site and/or B-site cations, unlocking new levels of compositional complexity and functional tunability. In this work, we investigate the impact of oxygen vacancies on the structural, electronic, and electrochemical properties of epitaxial $La(5B)O_3$ thin films, where 5B = $Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}$, synthesized by pulsed laser deposition (PLD). By systematically varying the oxygen partial pressure (P_O_2) during growth, we tune the oxygen vacancy concentration and investigate its influence on lattice structure, charge distribution, and surface oxygen evolution reaction activity. Comprehensive characterizations, including X-ray diffraction, scanning transmission electron microscopy, X-ray absorption spectroscopy, electrochemical measurements, and time-of-flight secondary ion mass spectrometry reveal a strong correlation between defects and water oxidation activity and stability. These findings highlight the potential of high-entropy oxide thin films as a platform for designing highly active and durable catalysts for water oxidation.

3:35PM – 3:50PM

From bulk to interface: solvent exchange and its role in interfacial model of magnesium batteries

Ying Chen[1], Rasha Atwi[2], Dan Thien Nguyen[1], J. David Bazak[1], Kee Sung Han[1], Nav Nidhi Rajpu[2], Nathan T. Hahn[3], Kevin R. Zavadild[3], Karl T. Mueller[1], Vijayakumar Murugesan[1]

[1]Pacific Northwest National Laboratory, [2]Stony Brook University, [3]Sandia National Laboratories

Multivalent battery chemistries have been explored in response to the increasing demand for high-energy rechargeable batteries utilizing sustainable resources. Solvation structures of working cations have been recognized as a key component in the design of electrolytes; however, most structure–property correlations of metal ions in organic electrolytes usually build upon favorable static solvation structures, often overlooking solvent exchange dynamics. Using multimodal NMR analysis and MD/DFT calculations, we determined the ion solvation structures and solvent exchange rates of magnesium electrolytes in various solvents, and revealed how the solvation structures and solvent exchange dynamics are correlated to the combined effects of several physicochemical properties of the solvents. Moreover, Mg^{2+} transport and interfacial charge transfer efficiency are found to be closely correlated to the solvent exchange rate in the binary electrolytes where the solvent exchange is tunable by the fraction of diluent solvents. Our primary findings are (1) most battery-related solvents undergo ultraslow solvent exchange coordinating to Mg^{2+} (with time scales ranging from 0.5 μs to 5 ms), (2) the cation transport mechanism is a mixture of vehicular and structural diffusion even at the ultraslow exchange limit (with faster solvent exchange leading to faster cation transport), and (3) an interfacial model wherein organic-rich regions facilitate desolvation and inorganic regions promote Mg^{2+} transport is consistent with our NMR, electrochemistry, and cryo-XPS results. This observed ultraslow solvent exchange and its importance for ion transport and interfacial properties necessitates the judicious selection of solvents and informed design of electrolyte blends for multivalent electrolytes.

4:10PM – 4:40PM Invited

Multivalent and complex ions at soft charged interfaces: Insights for Chemical Separations

Ahmet Uysal[1]

[1]Argonne National Laboratory

Chemical separations are crucial for refining and reprocessing critical materials such as platinum group metals, rare earths, and actinides. Typically during these processes, the target metal ions adsorb or transport across an aqueous interface, such as the solid/liquid interface in membranes and sorbents, and oil/water interface in liquid–liquid extraction (LLE). Despite the extensive use of these technologies over the decades, our understanding of the molecular-scale mechanisms behind ion adsorption and transport at the interfaces remains limited. This lack of knowledge poses a challenge in meeting the rising demand for these critical materials, which are increasingly used in advanced technologies. However, recent advancements in surface-specific experimental and computational techniques are promising in addressing this gap and potentially revolutionizing next-generation separation systems. Specifically, the complementary use of surface X-ray scattering and spectroscopy with vibrational sum frequency generation spectroscopy is a powerful approach to understanding interfacial ion–ion, ion–surfactant, and ion–solvent interactions. Several examples utilizing this approach to investigate multivalent and complex ions at charged interfaces will be highlighted.

4:40PM – 4:55PM

Imaging ion concentrations at magnetized interfaces for efficient separations of critical materials using Mach-Zehnder interferometry

Giovanna Ricchiuti,[1] Alan G. Joly,[1] Ivani Jayalath,[1] Yang Huang,[1] Grant E. Johnson,[1] Kevin Crampton,[1] Venkateshkumar Prabhakaran[1]

[1]Pacific Northwest National Laboratory

Measuring dynamic changes in ion concentrations is essential for uncovering the mechanisms of interfacial processes, including desolvation, enrichment/depletion, and charge transfer of targeted ions in chemical separations, synthesis, and energy conversion and storage technologies. Despite advancements in characterization and modeling approaches, establishing predictive structure-function correlations for specific events at interfaces remains challenging due to the insufficient lateral spatial and chemical resolution, which limits real-time visualization of ions. Mach–Zehnder interferometry (MZI) is an emerging spectroscopic technique that may be used to monitor and image the changes in ion concentrations in solution. In this work, we developed operando digital off-axis holography-based MZI to monitor the concentration of targeted paramagnetic critical metal cations (e.g., Nd^{3+}, Dy^{3+}, Ni^{2+}, and Co^{2+}) in aqueous solutions subjected to applied magnetic fields. When a magnetic field is applied, ions experience Lorentz and Kelvin forces based on their charge and magnetic susceptibility, causing them to move along the magnetic field gradient (magnetophoresis) and resulting in changes in the local refractive index of the solution. We built a digital off-axis holography-based Mach–Zehnder interferometer to monitor changes in the phase and refractive index. We converted phase changes into concentration maps, allowing us to directly visualize the formation of enrichment or depletion zones with targeted ions under a magnetic field. Our operando MZI capability will enable the rational design of efficient and selective electrode–electrolyte interfaces for separating critical materials, as well as energy conversion and storage.

4:55PM – 5:10PM

Harnessing Bubble Dynamics for Efficient Gadolinium Recycling and PFAS Preconcentration

Kaden Gravois,[1] Long Luo[1]

[1]Department of Chemistry, University of Utah

The increasing use of gadolinium (Gd)-based contrast agents in medical imaging and the environmental prevalence of per- and polyfluoroalkyl substances (PFAS) necessitate advanced preconcentration technologies. This study explores bubble-driven approaches to address these critical challenges.

For PFAS preconcentration, two bubble-mediated methods were developed. The first mimicked sea-spray aerosol enrichment using electrochemically generated H_2 and O_2 microbubbles, achieving ~1000-fold PFAS enrichment in 10 minutes as a complement to traditional solid-phase extraction (SPE). The second used shrinking CO_2/O_2 bubbles in an NH_4HCO_3 solution, enabling ~1400-fold enrichment in 20 minutes. Bubble bursting at the air–water interface generated aerosol droplets with surfactant-rich water layers, driving preconcentration. Shrinking bubbles improved efficiency by accelerating enrichment, while electrostatic interactions between the positively charged anode and negatively charged PFAS enhanced the process.

For Gd extraction, we developed a ligand-assisted electrochemical aerosol formation (LEAF) process that extracted ~75% Gd from µg/L-level hospital effluents, including diluted artificial urine, with a preconcentration factor of up to 390-fold. Surface-active Gd-binding ligands were essential, and their recyclability was demonstrated using an origami paper device under strong electric fields and steep pH gradients, achieving spatial separation of Gd and ligand.

These bubble-driven innovations provide scalable, environmentally friendly solutions for recycling Gd from hospital effluents and preconcentrating PFAS from water. They address pressing environmental challenges while advancing analytical and remediation technologies to meet global needs effectively and sustainably.

Posters

Poster flash talks

Tuesday, May 20th, 2025, 1:00 PM – 1:20 PM PST

Discovery Hall Horizon ABC

Moderator: Elias Nakouzi (Pacific Northwest National Laboratory)

Poster session

Tuesday, May 20th, 2025, 5:10 PM – 7:00 PM PST

Discovery Hall Horizon ABC

**Poster abstracts are grouped by topic

Abiotic and biologically-mediated nucleation, growth and dissolution

Peptoid nanotubular films as tunable scaffolds for directed calcium carbonate mineralization

Evan Angelo Mondarte,[1] Botao Hao,[1] Progyateg Chakma,[1] Alexander B. Bard,[1] Jinhui Tao,[1] Chun-Long Chen,[1] James J. De Yoreo[1]

[1]Pacific Northwest National Laboratory

In this study, we present an innovative utilization of assembled peptoid crystalline nanotubes formed into film coatings with tunable chemistries for $CaCO_3$ mineralization. Peptoid materials are gaining significant attention in biomaterials research due to their versatile chemical modifiability and exceptional stability, while retaining properties akin to biological materials. Through the modification of peptoid side-chain chemistries, we can facilitate the nucleation of calcium carbonate and direct the crystal formation process. We employed a combination of *ex situ* and *in situ* techniques, including SEM, AFM, and optical microscopy, to comprehensively investigate the crystallization process, accounting for variations in number densities, nucleation rates, and particle sizes across different peptoid tubular films. The formation of vaterite were observed for the two peptoid materials we investigated – one with -COOH groups in the hydrophilic domain (Pep1) and another one with $-NH_2$ groups (Pep2). Pep1 demonstrated a strong ability to promote nucleation, although it posed challenges for experimental methods to accurately quantify the system's interfacial energy. On the other hand, the Pep2-vaterite system exhibited an interfacial energy of 14 mJ/m^2 which is lower than other inorganic surface systems. The implications of these findings are substantial for the field of materials science, particularly in the realm of crystalline scaffold materials. We expect that through further modification of side chain group chemistries and distribution can provide a robust framework for designing materials that can accelerate $CaCO_3$ nucleation and in controlling the orientation of the resulting crystals.

Determining whether de-/re-mineralization or intergranular diffusion cause fluoride concentration gradients in human dental enamel

Jack Grimm,[1, 2] Katherine Tang,[1] Cameron Renteria,[1] Sandra D. Taylor,[2] Bojana Ginovska,[2] Arun Devaraj,[2] Dwayne D. Arola[1]

[1]University of Washington, [2]Pacific Northwest National Laboratory

Dental enamel is the most mineralized tissue in the body, composed of ~96% hydroxyapatite by weight in the form of ~50 × 100 nm nanocrystals. It must survive the mechanical and chemical challenges posed by the oral environment for decades. Cycles of demineralization by biofilm secretions and/or acidic dietary components alongside remineralization by calcium and phosphorous ions introduced by saliva put the composition of the outer enamel surface (OES) in constant flux. As excessive dissolution leads to caries formation and requires clinical intervention, fluorine substitutions are introduced to decrease the solubility of the hydroxyapatite. Fluorine is primarily incorporated in two ways: either during enamel formation or environmentally via exposure to e.g., fluoridated drinking water and dental treatments. The latter case is of particular interest as it is driven by daily exposures; the cumulative effects over decades result in higher fluoride concentration in senior enamel than young enamel. Environmental fluoride is naturally most strongly concentrated near the OES, but there remains a question about whether the fluoride is permanently incorporated into the nanocrystals, or merely stays in the intergranular phase separating nanocrystals which serves as a primary channel for diffusion. In this study, we apply atom probe tomography to *ex vivo* adult human enamel to determine whether the nanocrystals or intergranular phase are most responsible for the gradient in fluoride concentration as a function of distance from the OES. These results can provide guidance to improving the treatments that will minimize the risk of caries formation.

Understanding the formation mechanisms of biogenic manganese oxide todorokite

Ke Yuan,[1] Brian Sanders,[1] Barbara Evans,[1] Tomás Allen Rush,[1] Alyssa Carrell[1]

[1]Oak Ridge National Laboratory

Manganese (Mn) oxide minerals are found in diverse natural environments from Mn coatings on rocks to Mn nodules observed on the deep-sea floor. Todorokite, a unique tunnel-structured Mn oxide mineral has a wide range of applications in energy and environmental sciences. While abiotic synthesis of todorokite requires high temperatures, bacteria or fungi can produce todorokite in nature under ambient conditions, though the mechanisms remain elusive. This project aims to understand how microenvironments around the Mn-oxidizing bacteria/fungi could promote the direct nucleation or transformation of poorly crystalline Mn oxides to todorokite. We plan to use extracellular polymeric substances extracted from todorokite-producing and non-todorokite-producing bacteria or fungi to grow Mn oxides and compare that with minerals directly formed with the bacteria or fungi. I will present our preliminary results on the structure and morphology of Mn minerals formed through abiotic and biotic pathways. The principles uncovered here can inform the design of bio-inspired materials used for efficient growth of tunnel-structured Mn oxides and for the capture of heavy metals in aqueous environments.

Acknowledgment: Research sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy.

Biocement – Microbially Induced Immobilization Using Calcium Carbonate Precipitation

Miguel A Valdes[1]

[1]Pacific Northwest National Laboratory

Paenibacillus is a microbe that can produce carbonic anhydrase – an enzyme that encourages calcium carbonate precipitation in concrete/cement. Carbonic anhydrase catalyzes the formation of bicarbonate, which then reacts with calcium ions present in the environment – a reaction that takes place naturally in cement as it cures but is more efficient in the presence of this enzyme. Addition of carbonic anhydrase to cement yields a stronger, more carbonation resistant, product when compared to cement aged in the absence of the enzyme. This is facilitated by the formation of crystalline precipitates as a byproduct of enzymatic processes interacting with the alkaline environment found in cement pore spaces, filling pathways that would otherwise enable deleterious carbonation that leads to a more porous matrix. A gap in the literature is whether this technology is compatible with improving cementitious grouts of interest, like cast stone, or in reducing the leaching of contaminants such as nitrate from cementitious waste forms. The goal of this research is to study potential biocement recipes that may enhance cured and/or uncured cementitious materials of interest by sealing potential contaminant diffusion pathways by forming stable mineral phases in cement pores.

Emerging applications and tools for energy challenges

Dynamics of antifreeze glycoprotein as an inhibitor of natural gas hydrate growth

Dawson Bell,[1] Gabriel Miles,[1] Ran Drori, Konrad Meister, [1, 3] Oliviero Andreussi[1]

[1]Boise State University, [2]Yeshiva University, [3]Max Planck Institute for Polymer Research

Natural gas hydrates are crystalline water structures that form cages around trapped natural gas molecules. These hydrates, which typically form at low temperatures and high pressures, pose a challenge to the energy industry by clogging and damaging natural gas pipelines. Anti-freeze glycoprotein (AFGP) from *Dissostichus mawsoni* has been considered as an additive for inhibiting the growth of these hydrates. The protein is known for its ability to slow or prevent the growth of ice crystals, but experiments have shown it has substantial inhibitory activity on the growth of tetrahydrofuran (THF) hydrate as well. Furthermore, when AFGP is chemically modified with an isopropylidene group (AFGP-IPP), it has even greater activity than the wild-type molecule. Understanding the chemical mechanism of AFGP-IPP's enhanced activity could aid in intelligently designing synthetic inhibitors. To this end, we designed molecular dynamics simulations of the two AFGP variants binding to the surface of THF hydrate. Interactions with both the (001) surface and the (111) surface are examined. Enhanced-sampling via meta-dynamics is used to obtain an estimate of the free-energy profile as a function of the distance between key residues and the hydrate surface. The method of block-averaging is used to compute the error in our free energy estimates. Together, these methods are a robust strategy for studying how the free energy profile changes when the IPP modification is present.

Investigating coating strategies for enabling characterization of nanoparticles via atom probe tomography

Josephine Hartmann,[1] Chris McRobie,[1] Amy Hixon,[2] Sandra Taylor,[3] Alexander Bataller,[1] Kayla Yano,[3] Bharat Gwalani,[1] Daniel Perea,[3] Daniel Schreiber,[3] Elizabeth Kautz[1,3]

[1]North Carolina State University, [2]Notre Dame University, [3]Pacific Northwest National Laboratory

Atom probe tomography (APT) offers a unique capability to create three-dimensional maps of elemental and isotopic distributions for several material systems with near-atomic scale resolution. However, applying atom probe techniques to nanomaterials with complex geometries, such as nanoparticles or agglomerates, presents significant challenges. While several encapsulation methods for nanoparticles have been developed and reported, many of these approaches may not be versatile enough to accommodate the wide variety of nanoparticle sizes, shapes, and agglomerated structures which may be present over a range of energy and defense applications. Direct insights into the interfacial reactivity of nanoparticles can be particularly challenging to probe, requiring high resolution spatial and temporal information which APT can resolve. Here, magnetron sputtering systems were used to deposit thin films of Cr on Si substrates to evaluate these films for protective capping layers and encapsulation coatings for nanomaterials. Cr coatings deposited using two different sputtering systems (i.e., a DC magnetron sputtering system operating at a base pressure of 50 mTorr and a custom-built magnetron sputtering system with 8 mTorr base pressure) were compared. Depositing these Cr coating using an ‘underlayer’ and ‘overlayer’ strategy was then tested with iron oxide nanoparticles with varying sizes. Encapsulation effectiveness was investigated via imaging in STEM and APT data collection. The employment of these coating strategies can be related to post-detonation debris encapsulation which is of great interest related to national security, health, and environmental protection.

Impact of defect and Mg incorporation on structure and Magnetism in high-entropy spinel oxide films

Jueli Shi,[1] Le Wang,[1] Hsin-Mei Kao,[2] Mark E. Bowden,[1] Zihua Zhu,[1] Yingge Du[1]

[1]Pacific Northwest National Laboratory, [2]Oregon State University

High entropy spinel oxides provide an exciting platform for investigating the interplay between defects, cation diffusion, site occupancy, configurational entropy, and functional properties. In this study, we focus on the $(5A)_3O_4$ system (where $5A = Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}$) to examine the effects of oxygen vacancies and Mg incorporation on structural and magnetic properties. Using pulsed laser deposition, we systematically adjusted growth temperature and oxygen partial pressure to modulate oxygen vacancy concentrations and control Mg out-diffusion from the MgO substrate. Time-of-flight secondary ion mass spectrometry revealed the extent and spatial distribution of Mg diffusion across the film-substrate interface. Structural characterization by X-ray diffraction and scanning transmission electron microscopy provides insights into the lattice structure and local microstructure, while X-ray absorption spectroscopy demonstrate how oxygen vacancies and Mg incorporation influence the cation spin state, site occupancies, and the electronic band structure. These changes collectively modulate the magnetic properties of the films. This work highlights the intricate relationship between defect engineering, cation diffusion, and functional properties in high-entropy spinel oxides, offering valuable insights for designing advanced materials for magnetic and electronic applications.

Magnesium carbonates' growth rates on periclase/brucite surfaces exposed to environmental conditions using X-ray scattering methods

Pedro Josue Hernandez Penagos,[1] Emiliano A. Frayre Balderas,[1] Alan Delgado Romo,[1] Lawrence M. Anovitz,[2] Juliane Weber,[2] Jose L. Banuelos[1]

[1]University of Texas at El Paso,[2]Oak Ridge National Laboratory

Mineral looping using magnesium oxide (MgO, periclase) is a promising approach for direct air capture (DAC) of CO_2 from the atmosphere at the giga-ton scale and may help us meet our goals of reducing atmospheric carbon dioxide (CO_2) concentrations which affect global climate. The presence of humidity leads to the formation of $Mg(OH)_2$ (brucite), which grows over the MgO surface, forming a shell-like structure. The structure of this reaction layer may impact the overall carbonation yields. It is unknown how changing relative humidity levels will affect DAC using MgO, which currently impedes progress. In this work, batch experiments were conducted using MgO powder. These powders were exposed to relative humidity (RH) levels spanning 75% - 100% RH in a time series (up to 1-week reaction time). These samples were later exposed to CO_2 at varying temperatures ranging from 25 ˚C to 60 ˚C. Magnesium carbonate ($MgCO_3$) growth rates over mixed periclase/brucite surfaces were obtained from analysis of exposed samples. We will discuss small- and wide-angle x-ray scattering (SAXS & WAXS) results which describe $MgCO_3$ nucleation and growth kinetics.

Enhancing manganese dioxide cathode performance in aqueous batteries using internal magnetic fields

William McLeod,[1] Sireesha Pedaballi,[1] Jeffrey Bell[1]

[1]Washington State University

As the need for energy storage continues to rise, large bodies of research have been conducted on a variety of different electrochemical energy storage devices. Aqueous batteries fill a particular niche for low-cost, easy to manufacture, and safe energy storage despite their inferior performance compared to the more expensive, dangerous, and difficult to manufacture organic-based batteries, particularly lithium-ion batteries. Of all aqueous metal-ion batteries, the zinc-ion battery has garnered significant attention due to the abundance, low cost, and high theoretical capacity of zinc. Zinc-ion batteries use a variety of cathode materials, including organics, polymers, Prussian blue analogs, vanadium oxides, and most popularly manganese dioxide. While manganese dioxide has found success in this application, it remains plagued by solvation during cycling and irreversible intercalation of zinc ions, both of which contribute to rapid capacity fading over the battery's lifetime. In this work, we demonstrate how internal magnetic fields can enhance the operation of manganese dioxide cathodes in aqueous zinc-ion batteries. We employ permanent magnets incorporated in Swagelok cells to improve the capacity and capacity retention of the battery at no additional energy cost and with no additives to the electrode or electrolyte, preserving easy recyclability of the cells and magnets.

Frontiers in computation and advances in analytical techniques

Continuum Model for Simulating peptoid-mediated calcium carbonate nucleation

Yasmene Elhady,[1] Christopher J. Mundy,[1] Marcel Baer,[1] Bradley Harris[1]

[1]Pacific Northwest National Laboratory

Understanding peptoid-mediated calcium carbonate nucleation and growth is critical for designing novel carbon capture processes. We address the challenge of simulating these dilute systems with a hybrid computational approach that combines a modified Generalized Born (GB) continuum model with short-range corrections derived from all-atom potential of mean force (PMF) calculations. This method efficiently captures short-range interactions that are generally lost by continuum solvent simulations.

Anharmonic effects on material properties at high temperatures

Mal Soon Lee[1]

[1]Pacific Northwest National Laboratory

Ab initio molecular dynamics simulation technique is a promising tool to study various properties of vibrational spectra, X-ray absorption spectra, free energy, entropy, etc. even at high temperatures. With the harmonic phonon model, all interatomic forces are treated as purely harmonic so that the equilibrium distance between atoms is independent of temperature. At the low temperature regime, this model, commonly used in most quantum chemistry codes, can approximately model vibrational properties and free energetics. At higher temperatures, however, the harmonic model can break down since it cannot explain thermal expansion, where the role of anharmonicity becomes very important in the description and interpretation of the system. To better describe properties of systems at high temperatures, the quasi-harmonic approximation can be employed. In this presentation, I will discuss two examples of ethanol-adsorption in zeolites (catalysis) and electrocatalytic conversion of biomass derived organics at solid/liquid interface (electrocatalysis) to show how the quasi-harmonic approximation is used to rigorously evaluate the vibrational density of states at elevated temperatures. From this, the quantitative evaluation of thermodynamic properties such as entropy, enthalpy, free energy, and equilibrium constants can then be inferred.

Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies

Specific ions surface coverages on silica and adsorption free energies at pH 4 From nonlinear optics

Amani Alghamdi,[1] Alyssa L. Olson,[1] Franz Geiger[1]

[1]Northwestern university

We employ amplitude- and phase-resolved SHG experiments to probe interactions of fused silica:aqueous interfaces with Al^{3+}, Mg^{2+}, and Na^{+} cations at pH 4 and as a function of metal cation concentration. We quantify the second-order nonlinear susceptibility and the total potential in the presence and absence of 10 mM screening electrolyte to understand the influence of charge screening on cation adsorption. Strong cation:surface interactions are observed in the absence of screen electrolyte. The total potential is then employed to estimate the total number of absorbed cations. The contributions to the total potential from the bound and mobile charge were separated using Gouy-Chapman-Stern model estimates. All three cations bind fully reversibly, indicating physisorption as the mode of interaction. Of the isotherm models tested, the K_d adsorption model fits the data with binding constants of 3 to 30 mol^{-1} and ~300 mol^{-1} for the low (<0.1 mM) and high (0.1 -3 mM) concentration regimes, corresponding to adsorption free energies of -13 to -18 and -24 kJ mol^{-1} at room temperature, respectively. The maximum surface coverages are around 1013 cations cm^{-2}, matching the number of deprotonated silanol groups on silica at pH 4. Clear signs of decoupled Stern and diffuse layer nonlinear optical responses are observed and found to be cation specific.

A DFT study of Ra(II) and Ba(II) adsorption on montmorillonite surfaces

Jaeeun Kang,[1] *Wooyong UM*[1]

[1]POSTECH

Radionuclides such as radium (Ra) present in spent nuclear fuel pose significant challenges to the assessment of long-term disposal safety due to their high radiotoxicity. Direct investigation of the behavior of Ra is hampered by its inherent radiotoxicity and stringent handling requirements. Therefore, barium (Ba), a chemical analogue of Ra, is often adopted as a surrogate in studies. We employ density functional theory (DFT) to investigate the adsorption mechanisms of Ra(II) and Ba(II) on montmorillonite, a key component of engineered barrier systems in deep geologic repositories. Following identifying stable aqueous Ra and Ba complexes, their adsorption behavior on montmorillonite surfaces, (001) and (010) were investigated using VASP 6.3.0. Moreover, we simulated how the adsorption of Ra and Ba on the hydroxyl-rich (010) surface changed under different pH conditions. Our findings show that Ba exhibits lower adsorption energy than Ra on the (010) surface over a wide range of pHs, suggesting that Ba interacts strongly with the montmorillonite surfaces. However, on the (001) surface, $Ra(OH)_2(H_2O)_4$, exhibited lower adsorption energy than $Ba(OH)_2(H_2O)_4$, which is probably due to the difference in hydration energy. Furthermore, the charge density difference and density of states analysis provided a fundamental understanding of the Ba adsorption mechanism on montmorillonite, for predicting the long-term behavior of Ra in geological repositories. This study directly contributes to developing more effective engineered barrier systems and improving the long-term safety assessment of deep geological disposal.

A critical role of surface roughness on particle forces

Jaehun Chun,[1] R. Greg Felsted,[1] Jaeyoung Heo,[1] Alexander Bard,[1] Benjamin Legg,[1] Elias Nakouzi,[1] Gregory Schenter,[1] Jaewon Lee,[2] Peter Pauzauskie[3]

[1]Pacific Northwest National Laboratory, [2] University of Missouri, [3]University of Washington

Nanoparticles have been of great interest in both fundamental science and energy/environmental applications including crystal growth, solar cell arrays, and nuclear waste processing among many other examples. Understanding particle forces is central for collective responses and emergent phenomena such as adsorption and aggregation. However, it is challenging due to inherent coupling between physicochemical phenomena over different length and time scales. Here, we present our recent study for the effect of surface roughness on particle forces as a canonical example of scale coupling, specifically on van der Waals and hydrodynamic forces. The talk will show the critical importance of surface roughness on both energetics and dynamics of particles, providing in-depth understanding of various phenomena involving nanoparticles.

Interfaces under complex and extreme environments: High salinity, pH, temperature, confinement, radiation a

d photocatalysis

Reduced hygroscopicity slows metal silicate carbonation under low-water conditions

Bavan Rajan,[1] Sebastian T. Mergelsberg,[1] Mark E. Bowden,[1] Kelly A. Peterson,[1] Sarah D. Burton,[1] Geoffrey M. Bowers,[2] Thomas W. Wietsma,[1]Trent R. Graham,[1] Odeta Qafoku,[1] Christopher J. Thompson,[1] Sebastien N. Kerisit,[1] *John S. Loring*[1]

[1]Pacific Northwest National Laboratory, [2]St. Mary's College of Maryland

A solution for durable carbon storage involves injecting anhydrous CO_2 into basaltic geologic reservoirs. In the near term, water in the reservoir dissolves into the CO_2 to form a humidified supercritical fluid (sc-CO_2). Divalent metal silicate minerals in the host rocks react by dissolving into nanoconfined films of water adsorbed on their surfaces, and carbonate minerals precipitate to permanently trap CO_2. In this study, we investigated the underlying cause of a passivation effect unique to low-water conditions, where the carbonation of forsterite (Mg_2SiO_4) in thin water films slows significantly after ~10 h in humid sc-CO_2. We test the hypothesis that this passivation effect is due to a decrease in adsorbed water that facilitates forsterite dissolution and ion transport. Experiments were performed to follow the carbonation of forsterite as a function of total reaction time up to 5 days in sc-CO2, at 50 °C, 90 bar, and about 83% relative humidity. Integrated *in situ* and *ex situ* experimental demonstrate that the decrease in the forsterite carbonation rate correlates with a reduction in water film thickness, and in particular, weakly hydrogen-bonded adsorbed water that facilitates ion transport. We attribute the decrease in thickness to a drop in the concentrations of hygroscopic Mg^{2+} and HCO^{3-} ions within the film as the predominate forsterite carbonation product evolves from amorphous magnesium carbonate to magnesite ($MgCO_3$). This study furthers an understanding of divalent silicate carbonation under low-H_2O CO_2-dominated fluids as part of a comprehensive effort to predict the fate of CO_2 stored in geologic reservoirs.

Influence of basalt glass reactivity on carbon mineralization in Columbia River basalt

Emily Nienhuis,[1] Quin Miller,[1] Heath Stanfield,[1] Ross Cao,[1] Todd Schaef[1]

[1]Pacific Northwest National Laboratory

Mineralization of carbon dioxide in flood basalts is gaining traction as a means for secure and long-term geologic storage of carbon dioxide. Here, carbon dioxide is injected into the subsurface and subsequently reacts with the reservoir rock to form carbonate minerals. To enable accurate reservoir models capable of capturing the reactivity of basalt with carbon dioxide, the reactivity of each mineral phase must be parameterized, including that of the often-abundant glassy mesostasis. Glass is considered to be the most reactive portion of the basalt but is not well defined and left to estimation in current simulation efforts. Here, we utilize a series of synthetic basalt glasses and Columbia River hyaloclastite as basalt glass analogues to evaluate its relative reactivity compared to other minerals and the bulk rock reacted in aqueous dissolved CO_2 and supercritical CO_2 under subsurface-relevant conditions. Ultimately, we seek to place binding conditions on the factors controlling the reactivity of the basalt glassy mesostasis based upon glass composition and abundance for input into reservoir simulations to accurately predict the transport and fate of injected CO_2 in reactive basalt reservoirs.

Decoding the vibrational sum frequency generation spectra at air/ice and graphene/water interfaces

Richa Rashmi,[1] Francesco Paesani[1]

[1]University of California San Diego

Water molecules at interfaces exhibit distinct properties compared to those in bulk due to the disruption of the hydrogen-bond network by the phase boundary. This leads to dangling OH bonds with greater mobility and reactivity. In this study, we explore hydrogen bonding topologies at two physically relevant interfaces, air/ice and graphene/water, through vibrational sum frequency generation (vSFG) spectra calculated using path-integral quantum dynamics with the MB-pol many-body potential, underscoring the critical role of many-body interactions and nuclear quantum effects.

At the air/ice interface, water molecules form a quasi-liquid layer (QLL) with distinct properties from the bulk. We dissect the vSFG spectrum of the air/ice interface in terms of contributions arising from individual molecular layers, orientations, and hydrogen-bonding topologies to provide a realistic molecular picture of the evolution of the QLL as a function of temperature without the need for empirical adjustments. Notably, the emergence of specific spectral features suggests that surface restructuring may occur at lower temperatures.

At the graphene/water interface, the structure and dynamics of water significantly influence molecular responses to electric fields. Our quantum simulations reveal a distinctive dangling OH peak in the vSFG spectrum at neutral graphene, consistent with recent experimental findings. As the graphene surface becomes positively charged, interfacial water molecules turn away from the graphene, decreasing the intensity of the dangling OH peak. Remarkably, this charge-induced reorganization extends into deeper water layers, creating an unequal distribution of molecules with OH bonds pointing toward and away from the graphene sheet.

Finding infinities in nanoconfined geothermal electrolyte static dielectric properties and implications on ion adsorption/pairing

Kevin Leung[1]

[1]Sandia National Laboratories

Infinities should naturally occur in the dielectric responses of ionic solutions relevant to many geochemical, energy storage, and electrochemical applications at a strictly zero frequency. Using molecular dynamics simulations cross-referenced with coarse-grained Monte Carlo models, using nano-slit pore models at hydrothermal conditions, and treating confined mobile charges as polarization, we demonstrate the far-reaching consequences. The dielectric permittivity profile perpendicular to the slit ($\epsilon\perp(z)$) increases, not decreases, with ionic concentration, unlike in the more widely studied megahertz-to-gigahertz frequency range. In confined electrolytes, the divergences in $\epsilon\perp(z)$ correctly describe crossovers between bulk- and surface-dominated dielectric behavior. Nanoconfinement at low ionic concentrations changes monovalent ion energetics by 1−2 kJ/mol, but no dielectric property studied so far is universally correlated to ion adsorption or ion−ion interactions. We caution that infinities signal violation of the “electrical insulator” dielectric assumption. Finally, we present preliminary work on dielectric permittivity calculations of electrolytes inside cylindrical nanopores.

This work is based on materials support by the U.S. DOE Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under Field Work Proposal Number 21-015452 at Sandia National Laboratories. This article has been authored by an employee of National Technology & Engineering Solutions of Sandia, LLC under Contract No. DE-NA0003525 with the U.S. Department of Energy (DOE).

Theories for interface structure, dynamics, and charge transfer

Probing dynamics at mineral interfaces via non-equilibrium molecular dynamics

Bruce Palmer,[1] Pauline Simonnin,[1] Jaehun Chun[1]

[1]Pacific Northwest National Laboratory

This talk will describe viscosity profiles of electrolyte solutions near mineral interfaces. Non-equilibrium molecular dynamics simulations of flow in nano-channels constructed from mineral interfaces are performed. Based on the flow profiles in the channel, the viscosity profile can be reconstructed in a number of ways, including parabolic fits, splined-base fits and integration of the strain rate. The viscosity profiles near the interface can then be related to other structural properties such as density and concentration profiles. Results of simulations of different electrolyte solutions and different mineral surfaces will be presented.

Density functional theory calculations of CH_4 and CO_2 adsorbing to mineral surfaces

Lorena Tribe[1]

[1]Penn State Berks

Atomistic level calculations help shed light on the details of processes that occur at mineral interfaces and in interlayer spaces, providing visualizations for spaces that may be hard to probe with experimental techniques. The results can help shed light on structure and dynamics of surface complexes and include the potential for developing parameters for large-scale simulations. In this work, first principles molecular orbital-density functional theory was used to model two clay minerals, Na-montmorillonite and kaolinite, and their interactions with CH_4 and CO_2 molecules. Energy minimizations were performed followed by determination of the infrared vibrational frequencies. The free energies (ΔG) of adsorption of the clay models, the adsorbates, and the adsorbate-substrate clusters were determined, and the difference provided results for ΔG_{ads}. Selected input structures indicated that the presence of water molecules, modeled explicitly, lead to significant differences in

ΔG_{ads}. The outcomes depended strongly on the clay model (montmorillonite or kaolinite), the adsorbate, and the initial adsorbate-substrate cluster. The vibrational frequencies for adsorbed CO_2 were compared to experimental data and to calculations in the literature using molecular dynamics simulations. Energy scans for adsorbate moving away from the surface were performed to determine the activation energy finding a strong dependence on the position and nature of the surface complex as well as the number and distribution of the water molecules with respect to the surface.

Magnetic interactions between nanoscale domains in correlated liquids

Mohammadhasan Dinpajooh,[1] Giovanna Ricchiuti,[1] Andrew J. Ritchhart,[1]: Tao E. Li,[2] Sebastian T. Mergelsberg,[1] Venkateshkumar Prabhakaran,[1] Jaehun Chun,[1] Maria Sushko[1]

[1]Pacific Northwest National Laboratory, [2]University of Delaware

The formation of nanoscale domains (NDs) in correlated liquids and the emerging collective magnetic properties have been hypothesized as key mechanisms governing ion transport under external magnetic fields (EMFs). However, the molecular-level understanding of these magnetic field-driven phenomena and the interaction between these domains remain elusive. To this end, we introduce a simplified model of a solvated nanoparticle (NP) that consists of localized magnetic domains at their surfaces to represent groups of paramagnetic ions, forming NDs, whose effective magnetic dipole moments are at least one order of magnitude greater than the individual ions. We use classical density functional theory (cDFT) to estimate the effective interactions between these localized magnetic NPs (LMNPs). Our findings indicate that, unlike individual ions, magnetic dipole interactions of NDs in the LMNP model can indeed compete with the electrostatic, van der Waals, and hydration interactions. Depending on the direction of EMF, the cDFT effective interactions between two LMNPs turn out to become more attractive or repulsive, which may play a critical role in ion separation and nucleation processes. This indicates that the cDFT interaction barrier heights can be significantly affected by the magnetic dipole interactions and the barrier heights tend to increase as the size of LMNPs increases.

Computational study on structures of amelogenin under various conditions

Hoshin Kim,[1] Sebastian T. Mergelsberg,[1] Garry W. Buchko,[1] Bojana Ginovska[1]

[1]Pacific Northwest National Laboratory

Amelogenin plays a pivotal role in enamel formation in teeth by controlling the growth of woven hydroxyapatite (HAP), resulting in the hardest mineralized tissue in vertebrates. It is hypothesized that the primary to quaternary structures of amelogenin proteins directly influence enamel growth. However, a molecular-level understanding of the amelogenin structure and the mechanism of nucleation remains elusive. In this study, we investigated the structures of full-length murine amelogenin protein under different conditions, including the presence of a HAP interface and ions in solution. We conducted an extensive set of force-field-based classical molecular dynamics (MD) simulations, complemented by deep-learning-based structure prediction and statistical mechanics tools, to explore how ion concentration, pH, and the presence of HAP surface affect the rise of secondary and tertiary structures of amelogenin. Based on computationally predicted structures and their dynamics, we propose potential oligomeric structures formed through monomer self-assembly—an essential process for enamel

growth. The computed structural properties from MD simulations were compared with and validated against experimental data.

Wednesday, May 21, 2025 – Abstracts

Topic A : Theories for interface structure, dynamics, and charge transfer

Wednesday, May 21st , 2025, 9:00 AM – 11:35 AM PST

Discovery Hall Horizon A/B/C

Discussion Leaders: Jim Kubicki (University of Texas El Paso), Anastasia Ilgen (Sandia National Laboratories)

9:05 AM – 9:50 AM Keynote

Unraveling molecular structure and dynamics at aqueous interfaces with data-driven many-body quantum simulations

Francesco Paesani[1]

[1]University of California San Diego

Aqueous interfaces play a pivotal role in environmental and energy-related processes, driving phenomena such as catalysis, electrochemical reactions, and molecular recognition. Despite their significance, capturing the molecular-level structure and dynamics of these interfaces remains a formidable challenge due to the complexity of hydrogen-bonding networks. Leveraging our state-of-the-art data-driven many-body potentials, we have achieved unprecedented accuracy in modeling water across all phases. Using computational sum-frequency generation (vSFG) spectroscopy, our simulations have shed light on the structural and dynamical properties of various interfaces, including air/water, air/ice, and graphene/water interfaces. For the air/water interface, our simulations reproduce experimental vSFG spectra without empirical adjustments, revealing the interplay of many-body interactions and nuclear quantum effects in shaping hydrogen-bonding networks. At the air/ice interface, we dissect the quasi-liquid layer's molecular topology and its evolution with temperature, providing insights into surface melting. At graphene/water interfaces, we uncover the charge-induced reorganization of interfacial water molecules and its implications for energy storage and catalysis. These findings establish a new benchmark in the predictive modeling of aqueous interfaces, offering realistic insights into the underlying molecular interactions and mechanisms, advancing applications in energy, materials science, and environmental chemistry.

10:00 AM – 10:05 AM Session Introduction

10:05 AM – 10:35 AM Invited

Simulations of chemical reactivity at aqueous interfaces

Damien Laage[1]

[1]Ecole Normale Superieure

Chemical reactivity at aqueous interfaces exhibits profound differences from that in bulk solutions. While this is extensively used for heterogeneous catalysis at metallic interfaces, recent experiments have shown that even the simple air-water interface can facilitate reactions that are slow or unfavorable

in the bulk. This has opened promising avenues for green chemistry catalysis, particularly in aqueous microdroplets. Proposed explanations for these unique reactivities include the presence of dangling OH groups, large interfacial electric fields, and distinct solvation properties. However, a comprehensive molecular-level understanding remains elusive. We will show how reactive molecular dynamics simulations, using machine-learning potentials trained at the density-functional theory level and incorporating explicit nuclear quantum effects, provide detailed insights into interfacial reactivity. We will further show how these results can be generalized using analytic models to extend their applicability across varying system sizes. Applications of this approach will be illustrated for key interfacial chemical processes, including the surface acidity of water, the impact of interfaces on the Grotthuss mechanism of proton transport, and a critical step in the origins of life, the abiotic formation of peptide bonds.

10:35 AM – 11:05 AM Invited

Defects at Solid-Liquid Interfaces

Richard Remsing[1]

[1]Rutgers University

Chemistry at interfaces typically differs from that in the corresponding bulk phases. For example, catalysis often leverages unique properties of surfaces and interfaces to enhance chemical reactions. To understand chemistry at interfaces, we often consider idealized systems of a perfect crystalline solid in contact with a liquid solution. However, real systems are rarely perfect, and solids often contain defects like vacancies and trap states (electron/hole bound to a vacancy). These defects can serve as active sites where chemical reactions occur and can locally alter interfacial structure. Therefore, to understand and ultimately control chemistry at real solid-liquid interfaces, we need to build an understanding of how solid-state defects affect liquids and how liquids affect solid-state defects. I will discuss our efforts using theory and computer simulations to quantify how defects impact solvent effects that drive interfacial chemistry, and how defect patterning can be used to enhance reactivity. I will also discuss how liquids interact with and can alter the structure of electronic defects and implications for interfacial chemistry.

11:05 AM – 11:35 AM Invited

The Dynamic Reactivity of Carbonate-Water Interfaces at Far-From-Equilibrium Conditions

Paul Fenter[1]

[1]Argonne National Laboratory

Calcite, the most stable polymorph of $CaCO_3$, has been widely studied because of its importance as a mineral whose reactivity buffers pH and controls the transport of toxins in natural environments. While calcite's 'near-equilibrium' reactivity (i.e., dissolution, growth) has been well-studied (e.g., step flow, ion sorption), much less is known about its behavior in 'far-from-equilibrium' conditions. I will review our recent studies of the reactivity of $CaCO_3$ in acidic solutions containing dissolved Pb^{2+} that revealed several unexpected behaviors. Notably, the reactivity is highly sensitive to the polymorph of $CaCO_3$ (e.g., calcite, vaterite, and aragonite), the mineral grain shape/size, and the aqueous transport of reactants during reaction. Under some conditions, these reactions can lead complete mineral replacement of $CaCO_3$ by $PbCO_3$. These behaviors were understood through a suite of surface sensitive observations on well-defined calcite surfaces. Reactions in microfluidic cells to create well-defined fluid flow conditions revealed the development of complex surface topographies and spatially variable Pb-sorption patterns along the microfluidic channel. Operando observations also revealed the systematic inhibition of calcite dissolution by dissolved Pb^{2+}. The mechanisms underlying these behaviors were understood through in-situ observations of reacted calcite surface structure, revealing a novel Pb- incorporated interfacial structure that controls the observed reactivity of calcite.

*This work was funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Geosciences program under Contract DE-AC02-06CH11357 to UChicago Argonne, LLC as operator of Argonne National Laboratory.

Topic A : Theories for interface structure, dynamics, and charge transfer

Wednesday, May 21st, 2025, 1:00 PM – 4:50 PM PST

Discovery Hall Horizon A/B/C

Discussion Leaders: Franz Geiger (Northwestern University), Christopher J. Mundy (Pacific Northwest National Laboratory)

1:10 PM – 1:40 PM Invited

Lattice vibrations at interfaces probed by sum-frequency spectroscopy

Weitao Liu[1]

[1]Fudan University

Oxide/water interfaces host a wide range of important reactions in nature and modern industrial applications. However, accurate knowledge about these interfaces is still lacking at the molecular level due to difficulties in accessing buried oxide surfaces. In recent years, we have developed an experimental scheme enabling in situ sum-frequency vibrational spectroscopy of oxide surfaces in liquid water. Application to the silica/water interface revealed the emergence of unexpected surface reaction pathways with water, which helps resolve debates around the multimodal chemistry of aqueous silica discovered decades ago. Further studies unveil fresh information about isotopic effects, specific ion adsorption at the interface, and more, which complements our current understanding. Our study can provide new opportunities for future in-depth physical and chemical characterizations of other oxide/water interfaces.

1:40 PM – 1:55 PM

Accurate Solvation Free Energy Predictions via Neural Network Correction for Continuum Solvation Models

Bourgeois Gadjagboui,[1] Oliviero Andreussi[1]

Boise State University

The accurate prediction of solvation free energies is pivotal in computational chemistry, impacting drug discovery, materials science, and the study of chemical equilibria. Continuum solvation models are computationally efficient for these predictions but often fail to capture critical solute-solvent interactions, such as hydrogen bonding and solvent structuring, leading to significant errors in predictions for acids, bases, and ions. To address these limitations, we propose a hybrid approach combining classical molecular dynamics via thermodynamic integration with continuum solvation models and machine learning. Using a large dataset of solvation free energies, we define environment-based atomic descriptors (symmetry functions) and employ an atom-based neural network to systematically correct errors in continuum models. Our framework is expected to enable accurate solvation free energy predictions for molecules of diverse sizes, overcoming the limitations of existing models constrained to ~30 heavy atoms. This approach significantly enhances computational efficiency while offering deeper

insights into solute-solvent interactions, paving the way for broader applications in molecular property prediction.

1:55 PM – 2:10 PM

Water Orientation and its Energetics at Aqueous Si, Fe, Ni Oxide Interfaces from Nonlinear Optics

Franz Geiger[1]

Northwestern University

Fundamental investigations of metal oxide nanolayers and their applications for geochemistry and energy processes are presented. First, nonlinear optical laser spectroscopy reveals the number of net-aligned interfacial water molecules and the energetics associated with flipping them as a function of applied bias, ionic strength, and pH. Implications for strategies to lower the OER's overpotential are discussed. Second, nonlinear optical laser spectroscopy is employed to quantify the absolute surface coverages of geochemically relevant mono-, di-, and trivalent inorganic and organic ions at the silica/water interface. Implications for subsurface contaminant transport in heterogeneous geochemical environments are discussed. Science Adv., in press, and JPC A 2024, 128, 11, 2162-8.

2:30 PM – 3:00 PM Invited

Dielectric response of interfacial water

Dmitry Matyushov[1]

[1]Arizona State University

Dielectric response of a thin layer water is strongly reduced in the direction perpendicular to the substrate and is bulk-like in the direction parallel to the substate. The origin of this anisotropic susceptibility is the geometrical constraints imposed by the substrate on the mutual correlations of the interfacial water dipoles. This talks will discuss the dielectric response at the surface of spherical model solutes, planar biological membranes, and solvated proteins. Simple analytical theories can be constructed to represent both the results of recent measurements and simulations.

3:00 PM – 3:15 PM

Water Structure in Bulk and AlCl3 Interfaces: Insights from MD, X-ray, and SFG

Mohammadhasan (Hadi) Dinpajooh,[1] Biswajit Biswas,[2] Gwendolyn Gattermeir,[2] Elisa Biasin,[2] Narendra Adhikari,[2] John L. Fulton,[1] Shawn M. Kathmann,[1] Gregory K. Schenter,[1] Christopher J. Mundy,[1] Heather C. Allen,[2]

[1] Pacific Northwest National Laboratory, [2] Ohio State University

Aluminum (Al) in its ore form, bauxite, ranks as the second most mined metal following iron. Despite extensive research on aluminum's aqueous chemistry, the hydration and complexation of $AlCl_3$ in water, both in solution and at the air-water interface, are not well understood. This study delves into the water structure in aqueous AlCl$_3$ solutions under both bulk and interfacial conditions, utilizing X-ray spectroscopy, interface-selective sum frequency generation (SFG) vibrational spectroscopy, and molecular dynamics (MD) simulation. Extensive XRD and EXAFS analyses of bulk AlCl$_3$ electrolyte solutions reveal no evidence of contact Al^{3+} - Cl^{-} ion pairs, even at saturation concentrations. However, MD simulations using standard nonpolarizable force fields inaccurately predict contact ion pairing. By incorporating electronic polarization through mean-field charge rescaling, the issue is resolved, aligning MD simulations with experimental small-angle X-ray scattering (SAXS) measurements. Interface-selective SFG vibrational spectroscopy at interfaces also shows that Al^{3+} retains full hydration with no contact ion pairing or Cl^{-} complexation. The related MD simulations show Cl^{-} slightly approaches the surface layers with Al^{3+} positioned below. Across concentrations, SFG signals reveal disruption in hydrogen bonding, with maximum enhancement at 1.5 molal, indicating an expanded interfacial region. We propose that the SFG signal descriptor correlates with the water dipole potential or its projection which can be calculated from MD simulatio**ns.**

3:15 PM – 3:30 PM

Probing surface hydroxylation on metal ion adsorbed and doped aluminum oxyhydroxides

Zheming Wang,[1] Narendra Adhikari,[1] Mavis Boamah-Agyemang,[1] Xin Zhang,[1] Michel J. Sassi,[1] Carolyn I. Pearce, [1] Sue B. Clark, [2] Kevin M. Rosso,[1]

[1] Pacific Northwest National Laboratory, [2] Savannah River National Laboratory

Layered aluminum (oxy)hydroxides, such as gibbsite (Al(OH)$_3$) and boehmite (AlOOH) are important mineral phases in many industrial, geochemical and environmental processes. For these minerals, the structure and population of the surface hydroxyls greatly impact their chemical reactivities, and the former are expected to be affected by the extent of surface hydration and metal ion adsorption and incorporation. In this work we investigated the surface hydroxylation properties of synthetic gibbsite and boehmite nanoplatelets using vibrational sum frequency generation spectroscopy (VSFG) aided by other spectroscopy and microscopy techniques such as Raman and infrared spectroscopy, atomic force and electron microscopy and molecular dynamics simulations. We found that the VSFG spectra of pristine gibbsite resemble closely to its Raman spectra in the O-H stretch vibrational region under ambient conditions and further hydration has minimal effect on the energetics of the O-H vibration as reflected by the invariance of the VSFG spectra. However, for boehmite, the VSFG spectra varied dramatically from its Raman spectra due to the loss of strong H-bond interactions between the structural layers. We also found that metal ions (Cr^{3+}, Fe^{3+}, Re^{3+}, UO$_2{}^{3+}$) adsorption and incorporation leads to large variations of both the VSFG spectral intensities and profiles of gibbsite, indicating their strong effect on the surface O-H groups. However, The VSFG spectral changes are highly dependent on the specific metal ions and their concentrations. Possible mechanisms responsible for these spectral changes are discussed.

3:50 PM – 4:20 PM Invited

VASPsol++ - A nonlinear/nonlocal implicit electrolyte model for simulating solvated interfaces in VASP

Craig Plaisance,[1] Nkechi Kingsley,[1] SM Rewanul Islam,[1] David Ukuku[1]

[1]Louisiana State University

Current progress in the application of DFT to electrocatalytic processes is at least a decade behind compared to application of DFT to thermal catalytic processes due to the difficulty in modeling the electrochemical interface. While quantum mechanics is required to describe the bond breaking and formation processes occurring during electrocatalytic reactions, statistical sampling is also required to average over the vast configurational space of the electrolyte. This is particularly problematic when computing kinetic barriers for electrocatalytic processes since the transition state is often associated with the transport of charged species across the interface. We have recently implemented an improved implicit solvation model in the Vienna Ab initio Simulation Package (VASP), which we call VASPsol++. We have also developed a hybrid solvation method that combines both implicit and explicit treatment of water, allowing the inclusion of explicit water molecules where necessary to account for strong hydrogen bonding interactions as well as where required in the actual reaction mechanism such as for proton shuttling. We demonstrate the utility of the hybrid solvation method for computing kinetic barriers of electrocatalytic processes by examining several proton transfer steps that are relevant to CO_2 electrolysis. We compute the barrier as a function of electrode potential at both high and low pH, allowing the construction of computational Tafel plots. From these applications, we present a framework for using this method for the routine computation of kinetic barriers for electrocatalytic reaction steps.

4:20 PM – 4:35 PM

Kirkwood transitions and interfaces

Gregory Schenter,[1] Mohammadhasan Dinpajooh,[1] Shawn M. Kathmann,[1] Jaehun Chun,[1] Christopher J. Mundy[1]

[1]Pacific Northwest National Laboratory

Kirkwood transitions mark a qualitative change in ion correlation with concentration. In aqueous electrolytes, such changes in response can significantly impact phenomena at liquid/solid interfaces. This includes growth, transformation, stability, and particle-particle interaction. We will present new investigations of Kirkwood behavior as it influences such phenomena. We will present new theories and simulation techniques that will lead to the tuning and control of phenomena. A focus will be to bridge time and spatial scales, connecting molecular information to macroscopic continuum frameworks.

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, Condensed Phase and Interfacial Molecular Science programs Grant No. FWP 16249.

4:35 PM – 4:50 PM

Effects of surface strain on the electrochemical double layer

Collin Smith,[1] Gary Harlow[1]

[1]University of Oregon

In this study, RuO_2 (110) thin films were used to examine the impact of surface strain on the electrochemical double layer. By varying the film thickness, and in turn the extent of strain, the effects are examined through the potential of maximum entropy (PME) of the solid-liquid interface. Using the laser induced temperature jump method, the net orientation of solvent and charge present at the surface can be investigated, and the PME can be measured. The PME represents the potential where interfacial solvent is at it's highest entropy, leading to insights on how the electrode structure modifies the interface.

Topic B: Emerging applications and tools for energy challenges

Wednesday, May 21st, 2025, 1:00 PM – 4:50 PM PST

Discovery Hall D/E

Discussion Leaders: Anastasia Ilgen (Sandia National Laboratories), Udo Becker (University of Michigan)

1:10 – 1:40 PM Invited

Hydroxylation and carbonation of forsterite surfaces

Mavis Boamah-Agyemang,[1] John Loring,[1] Yifu Feng,[1] Xiaoxu Li,[1] Zheming Wang,[1] Kevin Rosso[1]

[1]Pacific Northwest National Laboratory

Hydroxylation and carbonation of mineral oxide are key for several processes in geochemistry and technological/industrial applications, such as remediation, catalysis, carbon storage, and dissolution. By investigating the vibrational structure of hydroxyl and carbonate groups present at interfaces of magnesium-based minerals, we will gain insight into reactivity to control and predict the interfacial chemistry that pushes industrial applications of these minerals. Forsterite (Mg_2SiO_4) is a promising candidate for insulation and biomaterial implants because of its unique mechanical characteristics and being highly considered for direct air capture for long-term carbon storage. Sum-frequency generation spectroscopy (SFG) provides the avenue to gain specific molecular-level information with high surface selectivity about how CO_2 reacts with forsterite in the presence of water from an interfacial perspective. First, we performed SFG studies at various relative humidities while nitrogen purging to learn how the forsterite surface hydroxylates. At 70% relative humidity and above, an intense broad peak centered around 3500 cm^{-1} appears in the spectra, which can be attributed to hydroxyl groups on the surface. However, the peak at 3500 cm-1 slowly disappears when relative humidity decreases from 90% to 0%. Secondly, we exposed forsterite surfaces to humidified CO_2; in addition to the hydroxyl peak, peaks likely from adsorbed CO_2, bicarbonate, and carbonate were observed on the surface. Atomic force microscopy reveals particles on the CO_2-treated forsterite surface that likely grew due to the reaction with CO_2. Insights from this study provide an avenue to overcome the passivation of Mg-based minerals during direct air capture.

1:40 – 1:55 PM

Substrate morphology and water availability influence interfacial structure in Mg-based mineral looping materials

Jose Leobardo Banuelos,[1] Pedro Josue Hernandez Penagos,[1] Alan Delgado Romo,[1] Emiliano Frayre,[1] Dong Youn Chung,[2] Elena Tajuelo Rodriguez,[3] Sai Adapa,[3] Lawrence M. Anovitz,[3] Andrew Stack,[3] Juliane Weber[3]

[1]The University of Texas at El Paso, [2]The Pennsylvania State University, [3]Oak Ridge National Laboratory

Though it is recognized that the hydroxylation reaction to form brucite on magnesium oxide (MgO) surfaces occurs quickly over a wide humidity range, the nucleation and growth of this phase has been less explored in nanoscale MgO substrates. Additionally, as MgO is currently being explored for its potential to realize efficient large-scale CO_2 direct air capture, the interplay of hydroxylation and carbonation reactions and structure of the resulting mineral phases must be understood. X-ray scattering-based characterization (SAXS/WAXS) reveals that even though high specific surface area (SSA) and high humidity result in fast brucite formation, these rates often plateau and take longer to reach full transformation compared to lower SSA MgO. Furthermore, the transformation to brucite involves metastable precursor phases that display up to three distinct interplanar spacings near the brucite (001) reflection, before converging to the brucite structure. Following the kinetics by analyzing the change in nanoparticle size and concentration offers a window into how confinement may limit reactant transport and ultimately demonstrate how the magnitude of the passivation effect depends on process conditions. We will discuss whether these phenomena present a challenge or opportunity for carbonate formation, and whether the sorbent can be regenerated without detrimental effects to the structure and CO_2 capture capacity.

1:55 – 2:10 PM

Theoretical insights into the dissolution of magnesium from hydrated forsterite crystal facets in humidified CO_2

Duo Song,[1] Sebastien Kerisit,[1] John Loring[1]

[1]Pacific Northwest National Laboratory

A comprehensive understanding of forsterite surface energetics and morphology at the atomic level is important for elucidating forsterite dissolution and carbonation mechanisms However, to our knowledge, even though dissolution of forsterite has been studied experimentally in significant details, only a few computational studies have addressed this issue. We present an *ab initio* study of the structure and surface energy at 0 K of the flat hydrated (010), (110), (001), (111), (021), (101) and (120) faces of forsterite using the DFT PBE Hamiltonian and a plane-wave basis set. According to the surface energy values, the stability order of the hydrated forsterite faces was found to be (010) < (110) < (001) < (111) < (021) < (101) < (120). The step energy of terrace-step $(0\bar{4}1)$ surface was investigated to study the energetics required to generate an active surface where the dissolution could occur. We propose an explanation accounting for these differences, by demonstrating that our results could provide crucial information on the forsterite dissolution mechanism with respect to its guest inclusions, a topic that is still under strong debate in the scientific community. Among all the facets, the terrace-step $(0\bar{4}1)$ surface is the least stable surface termination in water with convex Mg atoms in the outmost layer, suggesting dissolution of Mg atoms is the most likely to occur on the $(0\bar{4}1)$ surface when the outmost Mg atoms are bonded with ligands. We will show results for the energetics for dissolution of Mg from the $(0\bar{4}1)$ surface as a function of water film thickness in humidified CO_2 using metadynamics and nudged elastic band approaches.

2:30 – 3:00 PM Invited

Fatty amine monolayers: Molecular insights for efficient carbon capture

Eric Tyrode[1]

[1]KTH Royal Institute of Technology

When decorated with monolayers exposing specific functional groups, the air-water interface provides an environment with distinct physicochemical properties compared to the bulk. In the presence of chargeable moieties such as carboxylic acids or primary amines, the resulting surface charge and associated surface potential lead to significant variations in the local ion concentration, which can affect the apparent acid-base behavior and drive ion-specific interactions. Additionally, surface-bound functional groups can directly interact with gas-phase molecules. In this study, we examine fatty amine monolayers, providing a molecular-level understanding of their acid-base behaviour. The NH_2 group protonates with decreasing pH, but this equilibrium is altered at surfaces and interfaces. Using vibrational sum frequency spectroscopy (VSFS), an exquisite surface-sensitive technique, we track spectral features associated with the headgroup in its charged (i.e., NH_3^+) and uncharged (i.e., NH_2) states, along with interfacial water molecules, to elucidate key mechanistic details. Notably, we also investigate the influence of gas-phase CO_2 on the headgroup structure and orientation, as well as pH-dependent effects in the context of carbon capture. Our findings provide novel insights into the complex interplay between ions in solution, gas-phase molecules, and the technologically and biophysically relevant amine moiety.

3:00 – 3:15 PM

Probing carbonate and mineral film growth at complex interfaces

Kathryn Perrine[1]

[1]Michigan Technological University

Mineral carbonation has become the ideal method for CO_2 capture and storage, where alteration of materials increases CO_2 adsorption. Mineral film formation at complex interfaces in aqueous systems are influenced by several factors including, the type of ions and their concentration, pH, and surface sites. These processes involve redox processes and catalysis, which affect the growth rate and film structure. Our group developed a method to probe air/solution/iron interfaces simultaneously using *in situ* polarized modulated – infrared reflection absorption spectroscopy (PM-IRRAS). This technique allows for measuring vibrational signatures of film nucleation and growth in 3 stages: at the air/solution/metal interface, during gas adsorption at the liquid/solid interface, and air oxidation at the air/metal interface. Vibrational signatures of inorganic (mineral) films are shown to evolve and crystallize over time, as the interface becomes oxidized by adsorption of atmospheric CO_2 and O_2. Alkali and alkaline electrolytes on iron interfaces were investigated to compare how they affect CO_2 adsorption, film growth, and the production of surface sites through iron corrosion. We show how ions and solution pH influence surface corrosion, film identity, and rates. The competition between the cations and the dissolved iron from the surface on the rate of CO_2 adsorption to the air/solution/iron interface is also discussed. *In situ* atomic force microscopy (AFM) was used to measure the rate of apparent corrosion and surface morphology at different regions. These studies reveal the role of ions in the growth of mineral films impacting geochemical, environmental, and related interfacial processes.

3:15 – 3:30 PM

Isotopic fractionation at reactive mineral/electrolyte interfaces: Path-integral molecular dynamics perspective

Piotr Zarzycki[1]

[1]Lawrence Berkeley National Laboratory

Stable isotopic substitutions have served as tracers for equilibrium and kinetic processes in natural environments and in Earth's past. For example, the Earth's climate history and minerals diagenesis are primarily remonstrated based on the isotopic signature of light elements.

One of the most challenging questions regarding isotopic fractionation is the partitioning of isotopes between the solution and mineral phase and at the mineral/solution interface. These phenomena comprise an essential class of geochemical processes, and if understood, they can reveal the chemical conditions during mineral nucleation, growth, and geochemical evolution. Unfortunately, the experimental methods available to study the isotopic fractionation processes at the interface and monitor isotope composition during mineral growth are limited and not applicable to many mineral surfaces. We also lack a computational methodology to accurately predict isotopic fractionation in condensed phases – a gap addressed in this presentation.

Here, we will present the computation framework for calculating the equilibrium and kinetic isotopic fractionation of ions between the solution and mineral/electrolyte interface based on the Feynman path-integral formalism and compare it with the first-principle calculations beyond the Born-Oppenheimer approximation. We will focus on calcium and carbon fractionation between the $CaCO_3$ saturated solution and calcite (1014) surface. It remains one of the most challenging systems for which experiments and previous theoretical approaches contradict each other, and significant experimental uncertainties exist regarding the isotopic effects of carbonate minerals diagenesis.

3:50 – 4:20 PM Invited

Photocatalysts: Solar powered solutions to pollution and CO_2 reduction

Mary Jane Shultz,[1] Zhenyu Lin,[1] Rebecca Lynch,[1] Ziqing Xiong,[1] Emma Gubbin[1]

[1]Tufts University

Anatase titania photocatalysts are the subject of thousands of papers annually. Since the photo efficiency is low, doping TiO_2 photocatalysts with various elements is a widely employed technique to enhance performance. However, studies involving different catalyst sizes, morphologies, or dopants often yield varied or even contradictory conclusions. This contribution reports a versatile platform based on ultranano, < 2nm, particles (dubbed titanium ultranano particles, TiUNP), that minimizes defects, produces uniform morphology and enables systematic investigation of dopant control of product formation. Charge-carrier destination is determined by the dopant redox couple in the oxide matrix; a couple that is measured by diffuse reflectance spectroscopy. Versatility is demonstrated via doping with all fourth-period transition elements (except Sc). The dopant creates a local defect site; the defect can be leveraged to capture single-atoms of noble (Au, Pt, Ir, Pd) – or not so noble (Ni, Cu, W) – metals generating an environment that can reduce CO_2 in aqueous solutions.

For oxidation reactions, two distinct reaction pathways are identified; the balance between the pathways is regulated by the reduction potential of the dopant in the matrix. CO_2 reduction utilizes the reduction half reaction; products hinge on intermediate retention to support C-C coupling. Probing surface binding uses a recently invented nonlinear interferometer and TiUNP self-assembled on a substrate. The prospect for directing charge transfer significantly expands potential applications for titania.

4:20 – 4:35 PM

A unified framework for harnessing heat and light with hydrovoltaic devices

Tarique Anwar,[1] Giulia Tagliabue[1]

[1]EPFL

The conversion of ambient heat into electricity through natural evaporation presents a promising avenue for sustainable energy technologies. This study introduces a unified framework for Hydrovoltaic devices that transcends traditional mechanisms limited to ion movement near the solid-liquid interface. Our innovative strategy harnesses both thermodiffusion and photovoltaic effects to transform waste heat and solar energy into electrical power. Utilizing a top-evaporating surface in conjunction with a silicon-dielectric(core-shell) nanopillar array beneath a liquid layer, we report significant power output enhancements when exposed to external heat and solar irradiation. Crucially, our findings highlight that electricity generation relies not only on the movement of a polar solvent and ions across a narrow, partially wetted area of the top electrode but also on thermally and light-assisted ion migration, quantified by transfer capacitance in our proposed equivalent electrical circuit model. We demonstrate a state-of-the-art open circuit voltage of 1V and power density of $0.25W/m^2$ at high salinity. Moreover, we present the significant impact of material selection on device performance; for instance, transitioning from TiO_2 to Al_2O_3 dielectric shell results in voltage and power enhancements of 1.9 and 3.6 times at 25°C and 1.6 and 2.4 times at 70°C, respectively. Furthermore, high silicon doping leads to a 28% increase in open-circuit-voltage and a 1.6-fold gain in power output relative to low-doped samples. These findings provide crucial insights to enhance the device's efficacy, paving the way for broader operational strategies that consider environmental conditions, salinity, and interface engineering to optimize the harnessing of waste heat and sunlight.

4:35 – 4:50 PM

Transition metal dichalcogenides with double vacancies as catalysts for efficient CO_2 reduction to methanol

Denis Mulumba,[1] Md Khan Sharif,[1] Oliviero Andreussi[1]

[1]Boise State University

Global carbon dioxide (CO_2) emission has doubled and is projected to triple by 2040, highlighting the need for immediate strategies to address this rise. One promising approach involves the capture and conversion of atmospheric CO_2 into valuable chemicals in a sustainable and economical manner. Catalytic reduction of CO_2 to methanol has emerged as an attractive pathway. However, challenges

such as catalytic activity, selectivity and high operating temperatures limit the extensive use of this process.

Transition metal dichalcogenides (TMDCs), a class of two dimensional materials, have shown great promise as advanced catalysts for CO_2 reduction. Specifically, molybdenum disulphide (MoS_2), a member of TMDC family, exhibits nearly 94% methanol selectivity at 180 °C when a double vacancy is present in its structure. The introduction of such defects facilitates the selective dissociation of CO_2 enabling efficient methanol production.

Despite the excellent performance of MoS_2, the catalytic potential of other TMDC materials for CO_2 reduction, particularly with double vacancies, remains largely unexplored. In this study, we employed density functional theory based simulations to systematically investigate the catalytic performance of several TMDCs with double vacancies. We have evaluated their CO_2 catalytic conversion pathways which vary significantly due to the diverse local atomic environment within the double vacancies, ultimately influencing their catalytic activity and selectivity.

Thursday, May 22, 2025 – Abstracts

Topic A: Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies

Thursday, May 22nd, 2025, 9:00 AM – 11:35 AM PST

Discovery Hall Horizon A/B/C

Discussion Leaders: Kevin Rosso (Pacific Northwest National Laboratory), Nadine Kabengi (Georgia State University)

9:05 AM – 9:50 AM Keynote

Chemistry and impacts of oxide surfaces in air and water

Vicki Grassian[1]

[1]University of California San Diego

Oxide and silicate surfaces play key roles in technology and the environment as outlined in detail in a recent Chemical Reviews article.[1] These roles include as reactive components of mineral dust aerosol, as potential materials for solar radiation management and as environmental interfaces that control the fate and transport of biomacromolecules in aqueous systems. This talk will highlight some recent research advances in these areas as well as address some long-term research needs.

1. Leobardo Bañuelos, J.; Borguet,E.; Brown, G. E. Jr.; 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.; Lützenkirchen, 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" Chemical Reviews 2023, 123, 6413−6544."

10:05 AM – 10:35 AM Invited

Evaluation of quartz dissolution mechanisms and quartz-quartz interfaces with density functional theory

James D Kubicki,[1] Heath D. Watts[1]

[1]Earth, Environmental & Resource Sciences, The University of Texas at El Paso

Evaluating the mechanisms of quartz dissolution has been an active area of research for decades. For this work, we used density functional theory calculations at the M062X/6-311++G(d,p) level of theory to study quartz dissolution from a silicate cluster model ($Si_8O_{31}H_{31}Cl$). Full energy minimization calculations were performed on the models to evaluate a plausible reaction mechanism. The models included one with a protonated bridging O atom (i.e, $(H)O_{br}$) atom adjacent to a Q^1 -$Si(OH)_3$ group, hydration of that Q^1 Si group to form a pentavalent Si (O_{br}-$Si(OH)_3(OH_2)$) with an unprotonated O_{br}, one with both $(H)O_{br}$ and the $Si(OH)_3(OH_2)$ group, and one with unprotonated O_{br} and a non-hydrated -$Si(OH)_3$ group. Thermodynamics results of these reaction mechanisms are reported. In addition, the energy effects of increasing the Si-$(H)O_{br}$ bond length until dissolution of the $Si(OH)_3(OH_2)$ occurred are reported. The thermodynamics effect of the Cl^- proximity to the $(H)O_{br}$ link was examined. Calculations on the OH^--induced hydrolysis mechanism are also underway.

The nature of the quartz(101)-quartz(101) interface is also examined as a function of H_2O using periodic DFT calculations. The formation and interfacial energies are calculated for four different hypothesized interfaces.

10:35 AM – 11:05 AM Invited

Fluid-mineral-flow interactions: Pore-scale investigation of the influence of flow regimes on crystallization in porous media

Shaina Kelly,[1] Rosalie Krasnoff,[1] Olivia Terry,[1] Quin Miller,[2] Nabajit Lahiri,[2]

[1]Columbia University, [2]Pacific Northwest National Laboratory

This talk discusses pore-scale investigation of the influence of transport phenomena on supersaturation and crystallization in porous media, studied in geologic samples and 2D/3D microfluidic analogues. We highlight two studies that illustrate the influence of pore-scale morphology, partial saturation state (e.g., distribution of capillary water), and ion advection and diffusion on local crystal growth patterns. In the first study, computational fluid dynamics (CFD) methods are used to quantify steady-state water-CO_2 multiphase flow dynamics at different timescales in microCT images from subsurface vesicular basalt samples of varied alteration and pore connectivity. In particular, simulations of steady-state water-CO_2 partial saturation distributions, pH gradients, and ion sourcing within vesicles are spatially linked to carbon mineralization outcomes in post-CO_2 injection Columbia River Basalt samples from PNNL's Wallula injection pilot. In the second parallel study, 2D/3D microfluidics are used to investigate cooling-induced nucleation and crystallization behavior on laboratory timescales. Specifically, growth of $CuSO_4 \cdot 5\,H_2O$ crystals is studied with optical microscopy and microCT for different initial imbibition/drainage flow rates (unsteady-state) and steady-state continued flow or shut-in (i.e., diffusive regime). These experiments show that though minimization of crystal surface area to volume ratio is thermodynamically preferred, in systems that quickly evolve toward supersaturation state, crystal growth "dispersion" is greatly influenced by unsteady-state dynamics and shut-in time. Continued work will link geochemical dissolution and nucleation reactions at fluid-mineral interfaces to crystallization outcomes in flowing systems. Those connections will enhance understanding of transport-limited versus reaction-limited controls on crystallization for a variety of energy and environmental applications.

11:05 AM – 11:35 AM Invited

Exploring Interfacial Structure and Reactivity in Legacy Radioactive Tank Waste With IDREAM

Carolyn Pearce[1]

[1]Pacific Northwest National Laboratory

The Ion Dynamics in Radioactive Environments and Materials (IDREAM) Energy Frontier Research Center (EFRC) has uncovered new fundamental insights into precipitation and dissolution processes that are a grand challenge for processing radioactive tank waste at Hanford, a Department of Energy legacy plutonium production site. Hanford tank waste is complex and contains “sludge,” a mix of water-insoluble oxides/hydroxides of aluminum. IDREAM has elucidated the molecular mechanisms governing aluminum (oxy)hydroxide nucleation and crystal growth over a range of conditions and examined radiolytic water generation at their interfaces. Although gibbsite ($Al(OH)_3$) is known as the solubility-limiting phase across a wide pH range, its nucleation mechanism has been debated for decades. IDREAM examined dissolution of gibbsite in sodium hydroxide solutions using fast-scanning atomic force microscopy (AFM) and revealed that, in contrast to classical terrace-ledge-kink notions of monomer detachment, dissolution occurs by release of aluminate dimers that subsequently dissociate into monomeric species, which are the dominant species in solution. The continuous production of transient reactive species by ionizing radiation from radionuclides in the waste drives chemistry far from equilibrium. IDREAM investigated radiation effects with unprecedented spatial resolution using a unique AFM with an integrated X-ray source (RadAFM) to directly monitor radiolytically driven interfacial chemistry. Using these new capabilities, IDREAM has developed a foundation for understanding radiolytic products in Hanford solids and roles of adsorbed water and impurities at interfaces. For example, we have shown that simple carboxylates or chromium adsorbed on boehmite (AlOOH) nanoplates significantly slowed boehmite dissolution in alkaline solutions, despite incomplete surface coverage.

Topic A: Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies

Thursday, May 22nd, 2025, 1:00 PM – 3:20 PM PST

Discovery Hall Horizon A/B/C

Discussion Leaders: Nadine Kabengi (Georgia State University), Ke Yuan (Oak Ridge National Laboratory)

1:10 PM – 1:40 PM Invited

Oxidation pathways of UO_2 thin film under combined oxygen humidity-radiation conditions probed by XAFS

Xiaofeng Gu,[1] Juejing Liu,[1] Joanne Stubbs,[2] Peter Eng,[2] Steven Conradson,[1]

Aiping Chen,[3]

[1]Washington State University, [2]GeoSoilEnviroCARS, [3]Los Alamos National Laboratory

Understanding the uranium dioxide (UO_2) oxidation is of importance to minimize the environmental impact of fuel rod damage and leaking of uranium. Here, we studied the effect of water vapor, oxygen gas, and radiation on the surface oxidation of UO_2 (001) thin film. We in-situ observed the oxidation of UO_2 thin film in radioactive and anoxic/oxic environments with different humidity by utilizing grazing incidence X-ray absorption fine structure (XAFS). The XAFS result shows that in the anoxic environment, the combination of water vapor and X-ray radiation causes a distorted local environment for surface U, including generation of multiple U-O subshells, decrease of coordination number (CN) and shifting to shorter distances for U-U scatterings. The UO_2 in oxic environment exhibited further distortion than that of anoxic UO_2, such as increased number of U-O subshells and larger Debye-Waller factor for U-U shells. We hypothesis the oxidation in anoxic environment was driven by radiolysis of water molecules and formation of hydrogen peroxide. In oxic environment, oxygen gas not only directly oxidizes UO2 but also increasing the amount of H_2O_2 due to presence of more precure, HO_2●, by reaction between H● and O_2. This study showed that radiation play an important role in the oxidation of UO_2 surface, creating a pathway for further oxidation.

1:40 PM – 1:55 PM

Electrochemical/computational analysis of oxidation/reduction reactions of U_{60} and Pourbaix diagrams for adsorbed and incorporated species

Udo Becker,[1] Ben Gebarski[1]

[1] University of Michigan

Electrochemical analysis of U_{60} nanoclusters ($Li_{40}K_{20}[UO_2(O_2)(OH)]_{60}(H_2O)_{214}$) and their natural analog, the mineral studtite $(UO_2)O_2(H_2O)^2\cdot(H_2O)^2$, was carried out using cyclic voltammetry with a powder microelectrode setup. Voltammetric analysis was supplemented by *ab initio* quantum mechanical modeling to understand the mechanism, thermodynamics, and structural changes during redox transition (with a semi-quantitative kinetics evaluation). This research aims to better understand the redox behavior and transport of dissolved and incorporated uranyl units in the environment. Further

analysis is performed to determine if redox switching of actinyl ions in clusters can be performed while leaving the cluster intact or at what redox transition it disintegrates. Quantum-mechanical calculations were applied to approximate electrochemical peak potential shifts and add them to standard reduction potentials to more accurately assign peaks to specific redox transitions between different species. These peak potentials are calculated from oxidation state-dependent binding energies between different uranyl species either within or adsorbed to U_{60}. This theoretical approach incorporates extensive error cancellation and serves to predict electrochemical redox potentials and identify the reaction taking place. Voltammograms of U_{60} in electrolyte solutions exhibit kinetically-inhibited coupled redox peaks assigned to the U(VI)/U(V) transition of cluster structural uranyl units at -0.34 V (vs. standard hydrogen.

1:55 PM – 2:10 PM

Uranium reduction by magnetite: Mechanism of UO_2 formation from EELS analysis and density functional theory computations

Jacopo Carbone,[1] Barbora Bartova,[1] Thomas LaGrange,[1] Zezhen Pan,[2] Gregory Leinders ,[3] Rene Bes,[4] Nicolas Jacquemin,[1] Katharina Reinhold,[1] Michel Sassi,[5] Kevin M. Rosso,[5] Rizlan Bernier-Latman,[1]

[1] École Polytechnique Fédérale de Lausanne (EPFL), [2] Fudan University, [3] Belgian Nuclear Research Centre (SCK CEN), [4] University of Helsinki, [5] Pacific Northwest National Laboratory

In anoxic environments, the reduction of hexavalent uranium (U(VI)) to tetravalent U(IV) species results in its immobilisation through a decrease in aqueous solubility. The underlying reduction mechanism remains unknown but of critical importance to explain variability in U biogeochemical behaviors. This study focused on U(VI) reduction by the mixed-valence iron oxide magnetite (Fe_3O_4). The reduction ultimately yields crystalline uranium as $U(IV)O_2$. Investigations of the reduction mechanism revealed the emergence of uranium oxide nanocrystals, followed by their self-assembly into nanowires extending away from the magnetite surface. We suggest a reduction pathway initiated by U(VI) adsorption to the magnetite surface, forming pentavalent U(V). U(V) persists in UO_2+x nanoparticles that self-assemble into nanowires. Over time, the nanowires collapse, and uranium is fully reduced to tetravalent UO_2 nanocrystals. However, direct evidence for U(V) formation and persistence is lacking. Using electron energy loss spectroscopy (EELS), we analyzed O K-edge and U N-edge spectra of individual uranium oxide nanoparticles within nanowires. This enabled precise spatial characterisation of the uranium valence states by comparing the fine structures of nanoparticle-derived spectra with spectra from reference mixed valence oxides under identical conditions. Computational support is essential to validate reference spectra. We employed first-principles calculations to simulate the electronic structure and spectral characteristics of six uranium oxide phases with high accuracy, i.e., the single valence compounds $U(IV)O_2$, $KU(V)O_3$, $BaU(VI)O_4$ and the mixed valence compounds U_4O_9, U_3O_7, U_3O_8. By integrating computational models with experimental data, we aim to build a robust EELS dataset for investigating uranium redox transformations at the nanoscale.

2:20 PM – 2:50 PM Invited

Pore-scale confinement effects in hybrid resins optimized for treatment of multiple groundwater contaminants

Sarah Saslow[1]

[1]Pacific Northwest National Laboratory

Hybrid ion exchange (IX) resins have the potential to make groundwater cleanup at complex remediation sites more efficient by simultaneously removing multiple contaminants. Unlike single-contaminant selective IX resins, hybrid IX resins leverage IX and an additional removal mechanism, like reduction, precipitation, or adsorption, to remove different aqueous contaminants. One case study where hybrid IX resins are being explored as an alternative remediation technology is at the U.S. Department of Energy Hanford Site, where groundwater plumes for technetium-99 (Tc-99), uranium (U), hexavalent chromium (Cr(VI)), and iodine-129 (I-129) often overlap in the Central Plateau area. The 200 West Area pump-and-treat (200W P&T) facility currently uses single-contaminant selective IX resins to remove Tc-99 and U. However, expansion of 200W P&T operations could result in a wider range of contaminant concentrations, including Cr(VI) and I-129, to be processed through the facility. Recent laboratory studies have shown that a combination of two hybrid IX resins may be able to treat Tc-99, U, and Cr(VI) and incidentally remove I-129. For example, ResinTech, Inc.'s weak base hybrid resin SIR-700-HP can remove both U and Cr(VI) and their cerium hybrid resin, SIR-110-MP-Ce, can remove Tc-99 and some I-129. The mechanisms of interaction between U, Cr(VI), Tc-99, and their respective hybrid IX resins have been investigated, but knowledge gaps remain related to contaminant competition during treatment. The mechanism for I-129 removal by SIR-110-MP-Ce is less understood and is likely controlled by interactions between I-129 and Ce in the confined pore space environment typical of macroporous IX resins.

2:50 PM – 3:05 PM

Effects of Cs content in analcime-pollucite solid solution on morphology and Cs release

Seokju Hong,[1] Wooyong Um[1]

[1] POSTECH

Analcime-Pollucite solid solution (APSS, $Na_xCs_{1-x}AlSi_2O_6 \cdot xH_2O$) has been studied as the most suitable host material for the sequestration of radioactive Cs. The crystal structure of APSS does not release the sequestered Cs ions unless its aluminosilicate frameworks are completely destructed. The end-members of analcime ($NaAlSi_2O_6 \cdot H_2O$) and pollucite ($CsAlSi_2O_6$) have the same crystal structures. Thus, the APSS is known to have up to 42 wt% Cs sequestration capacity and its high Cs loading capacity is one of the benefits. Here, we carried out the Cs release test using 1 M KCl solution for 5 days. During the Cs release test, we found that the release of Cs from APSS exponentially increased when the Cs contents of APSS were 32 wt%. To investigate this unexpected high Cs release, we prepared end-members of analcime and pollucite, as well as the APSSs with Cs contents of 2, 4, 8, 16, and 32 wt%, respectively. All synthesized APSSs and end-member analcime showed euhedral truncated deltoidal icositetrahedron morphologies in the microscopic images. However, APSS with Cs content of 32 wt% showed a smaller crystal size (~5 μm) than other APSSs (~10 μm). Moreover, the end-member pollucite has been observed as particles with irregular morphology on the level of several tens of nanometers. This suggests that the Cs contents can affect the APSS crystal's morphology and size. In addition, the APSS crystal's morphology and size which are affected by the Cs content are considered to be directly related to the release of Cs.

3:05 PM – 3:20 PM

Predicting glass corrosion: From interfacial dissolution mechanisms to nuclear waste glass disposal

Sebastian Kerisit,[1] James J. Neeway,[1] Benjamin Parruzot,[1] Jarrod V. Crum,[1] Joelle T. Reiser,[1] Xuehang Song,[1] Yilin Fang,[1] Philip D. Meyer,[1] Gary L. Smith,[1] R. Matthew Asmussen,[1]

[1]Pacific Northwest National Laboratory

Immobilization of radionuclides through vitrification in borosilicate glass is a strategy pursued internationally for safe and long-term disposal of nuclear waste. Assessments of the potential long-term impacts on human health and the environment of disposal facilities rely in large part on the accuracy of nuclear waste glass corrosion models. Glass corrosion models need to account for the complex mechanisms of the interfacial glass-water reaction to enable reliable predictions of nuclear waste glass durability in disposal scenarios. Parameterization of such models is challenging and requires a quantitative understanding of the changes in corrosion behavior with time, reaction conditions, and glass composition. This presentation will provide a summary of the development, parameterization, validation, and application of a corrosion model for immobilized low-activity waste glass. This model combines a linear chemical affinity term to describe the approach to pseudo-equilibrium, a kinetic rate law to represent the ion-exchange reaction between protons in solution and alkali ions in the glass, and the formation of an alteration layer to account for incongruent dissolution. Laboratory tests that accelerate corrosion provide elemental releases as a function of reaction progress for model parameterization. Advanced solids characterization techniques are used to investigate dissolution mechanisms and validate model predictions. The glass corrosion model is then used in reactive transport simulations to predict the release of contaminants over the lifetime of a nuclear waste glass disposal facility (thousands of years).

Topic B: Interfaces under complex and extreme environments: High salinity, pH, temperature, confinement, radiation and photocatalysis

Thursday, May 22nd, 2025, 1:00 PM – 3:20 PM PST

Discovery Hall D/E

Discussion Leaders: Emily Nienhuis (Pacific Northwest National Laboratory) Benjamin Legg (Pacific Northwest National Laboratory)

1:10 PM – 1:40 PM Invited

Selective ion transport in solid confinement

Chong Liu[1]

[1]University of Chicago

Extremely selective separation exists in nature and is governed by a tailored dehydration process and transport pathway with a flat energy landscape. Restacked two-dimensional (2D) materials with Angstrom scale interlayer spacings represent a new platform to study water and ion transport in extreme confinement. Understanding the interplay between the confinement's structure, dimension, and surface chemistry is crucial to dialing the transport selectivity among competing ions. In this talk, I will present ion transport studies using 2D channels with dimensions less than 1 nm constructed from MoS_2 based materials. By changing the surface chemistry of MoS_2, we achieved control of channel dimension and the interaction between ions and the channels, resulting in the transport selectivity among cations. Furthermore, the coordination of cations and the complex ion interplay were shown to play a critical role in determining transport selectivity and anomalous behavior.

1:40 PM – 1:55 PM

Molecular Insights into Local Properties at Solid–Liquid Interfaces and Hydrodynamic Boundary Conditions for Confined Fluids

Haoyuan Shi,[1] Christopher J. Mundy,[1] Gregory K Schenter[1]

[1]Pacific Northwest National Laboratory

Confined fluids formed during the attachment and assembly of colloidal nanoparticles exhibit unique local physical properties, such as density, pressure, and viscosity, at solid–liquid interfaces. These fluids also show distinctive velocity profiles under pressure gradients when squeezed from confined spaces. Traditional continuum theories often lack the molecular-level resolution needed to capture these phenomena, as nanoscale hydrodynamic effects significantly impact boundary conditions and near-wall properties, resulting in the breakdown of the Stokes-Einstein relation. This study employs equilibrium molecular dynamics simulations to analyze the diagonal and off-diagonal components of the local stress tensor, linked to Harasima's formulations and Green-Kubo relations, alongside Bocquet and Barrat's hydrodynamic boundary condition theory. These molecular insights are integrated with continuum interpretations to explore the interplay between interfacial structures and hydrodynamic properties in shaping local fluid behavior. The results reveal two fluid layers near the wall with

diminished fluid-like behavior, characterized by significant fluctuations in local properties, which are excluded from the calculated hydrodynamic walls. This highlights how wall-fluid interactions influence local pressure, viscosity, and hydrodynamic slip, further impacting velocity profiles in confined systems under a pressure gradient. Additionally, strong interactions between the wall and ions affect the hydrodynamic boundary by reducing the slip length, referred to as "chemical roughness." Together with the physical roughness of the wall, these factors play a crucial role in influencing the local properties at solid–liquid interfaces. These findings provide a deeper understanding of the molecular mechanisms that govern macroscopic properties in confined fluids, advancing the connection between molecular-level behaviors and continuum-scale phenomena.

1:55 PM – 2:10 PM

Ion Retention and Repulsion in the Intervening Space Between Two Approaching Gibbsite Particles

Tuan Ho,[1] Hasini Senanayake[1]

[1]Sandia National Laboratories

In the aggregation of gibbsite particles in aqueous solutions, when one particle approaches another to a separation of just a few water layers, water and ions become confined in the narrow space between the particles. Under such nanoconfinement, ions may either be retained or expelled from the confined space. For a neutral basal gibbsite surface, stable under $pH < 10$, there are no electrostatic interactions between the ions and the surface according to Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. Instead, the equilibrium of ions between the confined space and bulk solution is influenced by ion interactions in a dielectric environment distinct from that of the bulk solution, as well as by ion-ion correlations. In this study, we applied molecular dynamics simulations to investigate the effects of ion-ion correlations on the free energy of ions in nanopores, compared to that in the bulk solution. Our results indicate that $Na+$ ions are likely to be expelled as the pore size decreases, while Cl^- ions are more likely to be retained. Na-Cl ion pairing enhances the retention of both ions in the nanopores. These findings suggest that nanoconfinement and ion pairing influence ion adsorption in nanopores, opening avenues for future research into how NaCl retention may affect particle-particle interactions, including oriented attachment, in aqueous solutions.

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2:20 PM – 2:50 PM Invited

Trends in Thermodynamics of Water Vapor Sorption in Alumina, Silica, and Imogolite Nanopores

Anastasia Ilgen[1]

[1]Sandia National Laboratories

Nanoconfined chemical environments, such as nanopores, are prevalent in natural settings like soils, rocks, and seafloor sediments. These environments significantly influence the behavior of chemical species due to their large surface-to-volume ratios, where surface interactions cannot be ignored. In particular, the nanoconfinement of solid-water interfaces can lead to novel hydrogen bonding structures, which impact ion solvation and the thermodynamics of chemical reactions in nanopores. Hydrogen bonding is the primary interaction mode between water molecules and oxide surfaces, such as silica and alumina. Therefore, to assess the energetics of hydrogen bonding interactions in the interfacial regions, we investigate the thermodynamics of water (H_2O) adsorption in cylindrical silica, alumina, and aluminosilicate (imogolite) nanopores with diameters ranging from approximately 2 nm to 7 nm. We find that in silica, H_2O adsorption is exothermic, with the exothermicity increasing as pore diameter decreases, indicating stronger hydrogen bonding interactions between water molecules and pore surfaces as pore diameters decrease. However, this trend is not universal; for imogolite with either hydrophobic or hydrophilic surface groups inside nanotubes, H_2O adsorption exhibits both exothermic and endothermic trends at low surface coverages, highlighting the influence of material characteristics and confinement on adsorption behavior. The thermodynamic findings regarding H_2O adsorption on porous and non-porous silica, alumina, and imogolite will be discussed. These findings have implications for the behavior of water in unsaturated zones (e.g., soils), where H_2O vapor is one of the primary phases of water and where there is an abundance of nanopores.

2:50 PM – 3:05 PM

Resolving intermediates during nucleation and growth of gibbsite promoted by laser irradiation

Emily Nienhuis,[1] Xiaoxu Li,[1] Ashley Kennedy,[1] Hsiu-Wen Wang,[1] Zheming Wang,[1] Lili Liu,[1] Jim De Yoreo,[1] Kevin Rosso,[1] Carolyn Pearce[1]

[1]Pacific Northwest National Laboratory

The mechanisms and kinetics associated with nucleation and growth of gibbsite from concentrated alkaline aluminate solutions are poorly understood and not captured by current models. This is especially apparent in complex solutions representative of nuclear tank waste, where the processes behind gibbsite nucleation and growth are further convoluted by limited waters of solvation and exposure to ionizing radiation. In the current work, we produced a series of metastable sodium aluminate solutions containing different ratios of aluminum, sodium, hydroxide, and water to control precipitation timelines and capture intermediates involved in the early stages of gibbsite nucleation and growth. We then deposited energy into these solution systems via laser irradiation to determine if radiation effects can provide alternative pathways or change the kinetics of gibbsite nucleation and growth. Using cryogenic transmission electron microscopy and energy dispersive X-ray spectroscopy, we compared the size, morphology and chemistry of the nucleating particles as a function of solution composition and time, and in the presence and absence of laser irradiation. These snapshots allowed us to unravel the complex processes by which gibbsite is precipitated from concentrated alkaline

aluminate solutions. An understanding of this mechanism is an important step in gaining predictive control of these systems for nuclear waste management.

3:05 PM – 3:20 PM

Two-dimensional infrared spectroscopy of aqueous structure and dynamics in high salinity, high pH environments

Robert Felsted,[1] Trent R. Graham,[1] J. David Bazak,[1] Sebastian T. Mergelsberg,[1] Carolyn I. Pearce,[1] Zheming Wang,[1] Kevin Rosso[1]

[1]Pacific Northwest National Laboratory

Water-ion interactions influence the physicochemical properties of solutions, having impacts on solution structure, dynamics, and rheological properties. These interactions are particularly impactful in extreme environments such as high salinity and high pH solutions, and information on water-ion interactions in such environments can be gained through ultrafast two-dimensional infrared spectroscopy (2D-IR). 2D-IR spectroscopy provides information on the femtosecond timescale about molecular-level dynamics and solution structure by observing vibrational frequency correlation and vibrational energy transfer over time. We used 2D-IR spectroscopy of a thiocyanate probe molecule to analyze solution dynamics in high concentration lithium salt solutions, including LiCl, LiBr, $LiNO_2$, and $LiNO_3$. Analysis of the dynamics reveals that $LiNO_2$ shows more than 30% longer correlation times compared to other lithium salt solutions, indicating that concentrated LiNO2 significantly enhances solution ordering. Additionally, we used 2D-IR to analyze dynamics of a selenocyanate ($SeCN^-$) vibrational probe in alkaline D_2O solutions and to observe vibrational energy transfer from the $SeCN^-$ anion to an OD^- anion. The rate of energy transfer from the $SeCN^-$ anion is not proportional to the concentration OD^- anions, as a stochastic model of ion distribution would predict. Instead, analysis of vibrational energy transfer and dynamics indicates formation of solution ordering at concentrations well below 1 M NaOD. Results from these experiments provide insight into solution behavior under extreme conditions particularly relevant to low hydration, high alkalinity systems.

APPENDIX V: Program book

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MAY 19–23, 2025

Interfaces for Energy and the Environment Conference

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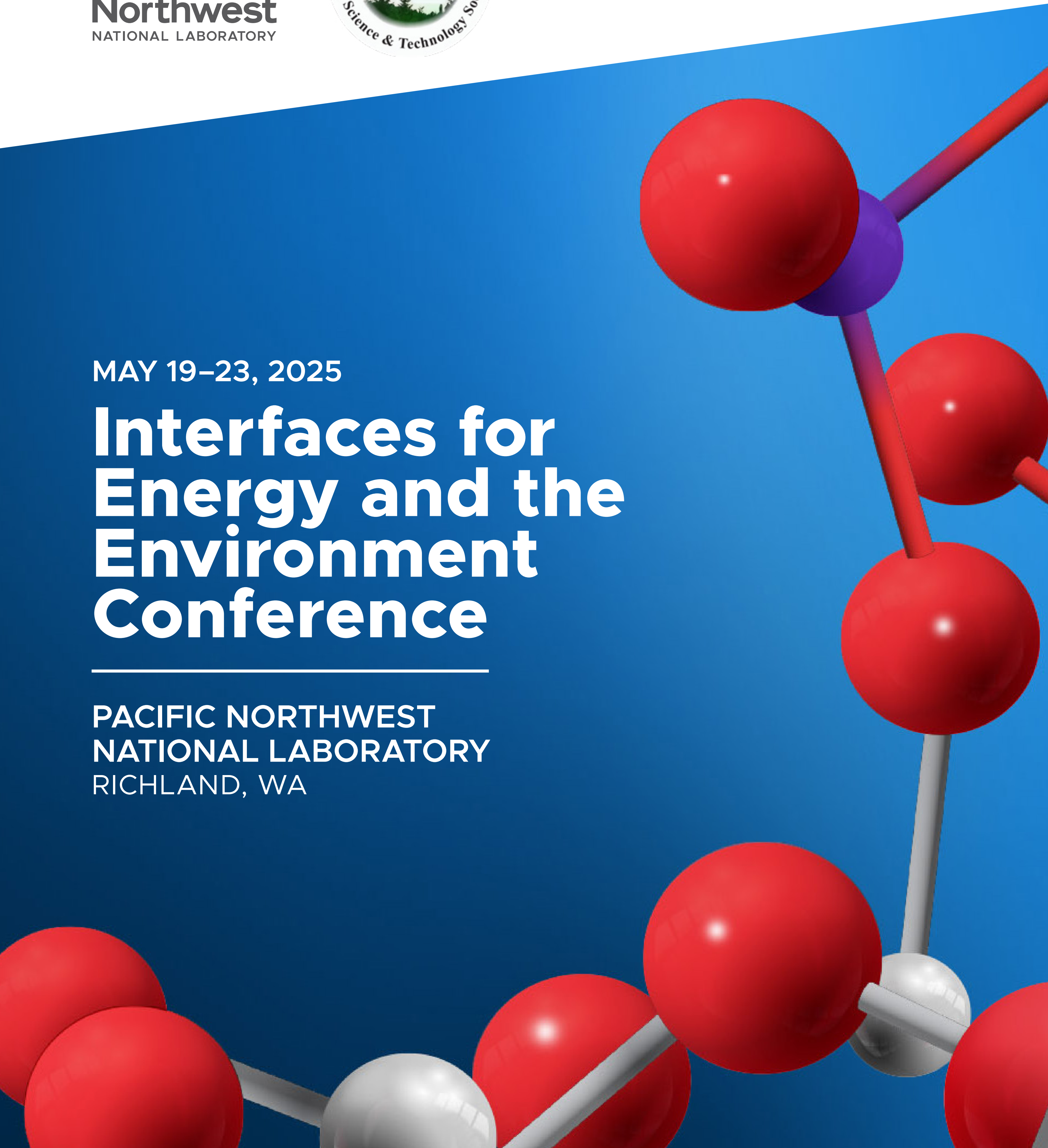

WELCOME TO THE 2025 IEEC

On behalf of the organizing committee, we warmly welcome you to Pacific Northwest National Laboratory for the 2025 Interfaces for Energy and the Environment Conference (IEEC). We are thrilled to offer this first-of-its-kind conference, connecting scientists and engineers all working on various aspects of interfacial science for energy and environmental applications. We hope all of you find the sessions stimulating and that you have ample opportunities to create, renew, and deepen friendships and collaborations.

Thank you very much for your participation and contributions, making this conference not only possible but also a great success.

CONFERENCE CO-CHAIRS:

Sandra Taylor, PhD
Pacific Northwest National Laboratory
sandra.taylor@pnnl.gov

A geochemist, Sandra's research focuses on understanding crystal growth mechanisms across a broad range of fields—from biogeochemistry to corrosion science to novel materials synthesis—using advanced microscopy techniques.

Sandra Taylor, PhD

Mavis Boamah, PhD
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An experimental geochemist, Mavis specializes in probing interfacial chemistry and electron transfer processes at mineral–aqueous and mineral–organic interfaces. Her research leverages ultrafast spectroscopy techniques to advance solutions in water remediation, electronic nanodevices, geochemical systems, critical materials separations, and renewable energy technologies.

Mavis Boamah, PhD

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AGENDA AT A GLANCE

MONDAY, MAY 19, 2025

MORNING SESSIONS
PNNL, RICHLAND, DISCOVERY HALL (ABC)

TIME	TOPIC
9:00 a.m.	Welcome Remarks
9:10 a.m.	Session Topic: Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies
9:15 a.m.	Keynote: Rachel Segalman, Using bio-inspired polymers to understand water-surface interactions
10:00 a.m.	**Networking Break**
10:15 a.m.	Invited Talks: Jenée Cyran, Benjamin Legg, Juliane Webber
11:45 a.m.	Introductory Remarks: Steven Ashby, Lab Director, PNNL
12:00 p.m.	**Lunch (provided)**
1:00 p.m.	Poster Flash Talks

AFTERNOON SESSIONS
PNNL, RICHLAND, DISCOVERY HALL (ABC OR DE)

TIME	TOPIC
1:20 p.m.	Session Topic (Discovery Hall ABC): Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies
1:20 p.m.	Session Topic (Discovery Hall DE): Abiotic and biologically-mediated nucleation, growth and dissolution
1:30 p.m.	Invited/Contributed Talks I Discovery Hall ABC: Benjamin Gilbert, Melese Getenet, Md Mosfeq Uddin
1:30 p.m.	Invited/Contributed Talks I Discovery Hall DE: Young-Shin Jun, Xinyi Shen, Maria Sushko
2:30 p.m.	**Networking Break**
2:50 p.m.	Invited/Contributed Talks I Discovery Hall ABC: Anju Gupta, Gary Harlow, Krishan Kanhaiya
2:50 p.m.	Invited/Contributed Talks I Discovery Hall DE: Sandra Taylor, Xin Zhang, Yuna Bae
3:50 p.m	**Networking Break**
4:10 p.m.	Invited/Contributed Talks I Discovery Hall ABC: Hilary Emerson, Nefeli Bompoti, Thomas Underwood
4:10 p.m.	Invited/Contributed Talks I Discovery Hall DE: Elias Nakouzi, Mingyi Zhang, Marlo Zorman
5:10 p.m.	Poster Session and Vendor Exhibit

AGENDA AT A GLANCE

TUESDAY, MAY 20, 2025

MORNING SESSIONS
PNNL, RICHLAND, DISCOVERY HALL (ABC)

TIME	TOPIC
9:00 a.m.	Session Topic: Frontiers in computation and advances in analytical techniques
9:05 a.m.	Keynote Two: Mischa Bonn, A molecular view of water interfaces
9:50 a.m.	**Networking Break and Vendor Exhibit**
10:05 a.m.	Invited Talks: Simone Pezzotti, Satoshi Nihonyanagi, Kevin Rosso
11:35 a.m.	**Lunch (provided): Optional Memoriam Session**
1:00 p.m.	Poster Flash Talks

AFTERNOON SESSIONS
PNNL, RICHLAND, DISCOVERY HALL (ABC OR DE)

TIME	TOPIC
1:20 p.m.	Session Topic (Discovery Hall ABC): Frontiers in computation and advances in analytical techniques
1:20 p.m.	Session Topic (Discovery Hall DE): Emerging applications and tools for energy challenges
1:30 p.m.	Invited/Contributed Talks I Discovery Hall ABC: R. Kramer Campen, Raiden Speelman, Jacob Filser
1:30 p.m.	Invited/Contributed Talks IDiscovery Hall DE: Sara E. Mason, Chris Young, Rebecca Anderson
2:30 p.m.	**Networking Break and Vendor Exhibit**
2:50 p.m.	Invited/Contributed Talks I Discovery Hall ABC: Eric Borguet, Nicole Gonzalez, Shawn Kathmann
2:50 p.m.	Invited/Contributed Talks I Discovery Hall DE: Mario Villalobos, Le Wang, Ying Chen
3:50 p.m.	**Networking Break and Vendor Exhibit**
4:10 p.m.	Invited/Contributed Talks I Discovery Hall ABC: Hendrik Heinz, Juejing Liu, Sten Lambeets
4:10 p.m.	Invited/Contributed Talks I Discovery Hall DE: Ahmet Uysal, Giovanna Ricchiuti, Kaden Gravois
5:10 p.m.	Poster Session and Vendor Exhibit

AGENDA AT A GLANCE

WEDNESDAY, MAY 21, 2025

MORNING SESSIONS
PNNL, RICHLAND, DISCOVERY HALL (ABC)

TIME	TOPIC
9:00 a.m.	Session Topic: Theories for interface structure, dynamics, and charge transfer
9:05 a.m.	Keynote Three: Francesco Paesani, Unraveling molecular structure and dynamics at aqueous interfaces with data-driven many-body quantum simulations
9:50 a.m.	**Networking Break and Vendor Exhibit**
10:05 a.m.	Invited Talks: Damien Laage, Richard Remsing, Paul Fenter
11:35 a.m.	**Lunch (provided) Optional Team Building Hour**

AFTERNOON SESSIONS
PNNL, RICHLAND, DISCOVERY HALL (ABC OR DE)

TIME	TOPIC
1:00 p.m.	Session Topic (Discovery Hall ABC): Theories for interface structure, dynamics, and charge transfer
1:00 p.m.	Session Topic (Discovery Hall DE): Emerging applications and tools for energy challenges
1:10 p.m.	Invited/Contributed Talks I Discovery Hall ABC: Weitao Liu, Bourgeois Biova Irenee Gadjagboui, Franz Geiger
1:10 p.m.	Invited/Contributed Talks IDiscovery Hall DE: Mavis Boamah-Agyemang, Jose Leobardo Banuelos, Duo Song
2:10 p.m.	**Networking Break and Vendor Exhibit**
2:30 p.m.	Invited/Contributed Talks I Discovery Hall ABC: Dmitry Matyushov, Mohammadhasan Dinpajooh, Zheming Wang
2:30 p.m.	Invited/Contributed Talks I Discovery Hall DE: Eric Tyrode, Katheryn Perrine, Piotr Zarzycki
3:30 p.m.	**Networking Break and Vendor Exhibit**
3:50 p.m.	Invited/Contributed Talks I Discovery Hall ABC: Craig Plasisance, Gregory Schenter, Collin Smith
3:50 p.m.	Invited/Contributed Talks I Discovery Hall DE: Mary Jane Shultz, Tarique Anwar, Denis Mulumba
6:00 p.m.	Dinner Banquet: Fiction @ J. Bookwalter Winery, 894 Tulip Ln, Richland, WA 99352

AGENDA AT A GLANCE

THURSDAY, MAY 22, 2025

MORNING SESSIONS
PNNL, RICHLAND, DISCOVERY HALL (ABC)

TIME	TOPIC
9:00 a.m.	Session Topic – Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies
9:05 a.m.	Keynote Four - Vicki Grassian: Chemistry and impacts of oxide surfaces in air and water
9:50 a.m.	**Networking Break**
10:05 a.m.	Invited Talks: Jim Kubicki, Shaina Kelly, Carolyn Pearce
11:35 a.m.	**Lunch (provided)**

AFTERNOON SESSIONS
PNNL, RICHLAND, DISCOVERY HALL (ABC OR DE) OR ESC

TIME	TOPIC
1:00 p.m.	Session Topic (Discovery Hall ABC): Interfaces under complex and extreme environments – High salinity, pH, temperature, confinement, radiation and photocatalysis
1:00 p.m.	Session Topic (Discovery Hall DE): Interfaces at all scales: Extending the spatial and temporal scales of interfacial studies
1:10 p.m.	Invited/Contributed Talks I Discovery Hall ABC: Chong Liu, Haoyuan Shi, Tuan Ho
1:10 p.m.	Invited/Contributed Talks I Discovery Hall DE: –, Udo Becker, Jacopo Carbone
2:10 p.m.	**Networking Break**
2:20 p.m.	Invited/Contributed Talks I Discovery Hall ABC: Anastasia Ilgen, Emily Nienhuis, Robert Felsted
2:20 p.m.	Invited/Contributed Talks I Discovery Hall DE: Sarah Saslow, Seokju Hong, Sebastien Kerisit
3:20 p.m.	**Networking Break I Travel to ESC**
3:45 p.m.	Poster Awards
4:20 p.m.	Networking Break
4:40 p.m.	Honoree Panel

FRIDAY, MAY 23, 2025
8:30 A.M. – OPTIONAL LAB TOUR: MEET IN ESC LOBBY

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GEOC Symposia at the ACS Fall 2025 Meeting in Washington, DC

Join us at the ACS Fall 2025 Meeting from August 17 to 21, where the Geochemistry Division will host eight exciting sessions. Explore topics such as:

- *Biogeochemistry of Phosphorus*
- *Recovery and Recycling of Critical Materials*
- *Interfacial Structure and Reactivity in Mineral–Water Systems*
- *General Geochemistry*
- *Extraction Sustainability of Technology-Critical Minerals*
- *Methane: Policy for a Greenhouse Gas*
- *Mineral Crystallization, Aggregation, and Dissolution*
- *Transport, Wettability, and Geochemistry in Tight Rocks*

Call for Symposia for the ACS Spring 2026 Meeting in Atlanta, GA

The ACS Geochemistry Division invites proposals for symposia at the ACS Spring 2026 Meeting, scheduled for March 22-26, 2026, in Atlanta. Proposals are due tentatively by July 7th, 2025. Contact GEOC program-chairs, Ian C. Bourg (bourg@princeton.edu) and Vitalii Starchenko (vsv@ornl.gov) for details.

For more information, please contact the division chair, Sang Soo Lee (sslee@anl.gov) and secretary, Qingyun Li (qingyun.li@stonybrook.edu) or visit the ACS-GEOC website (https://www.acsgeoc.org/).

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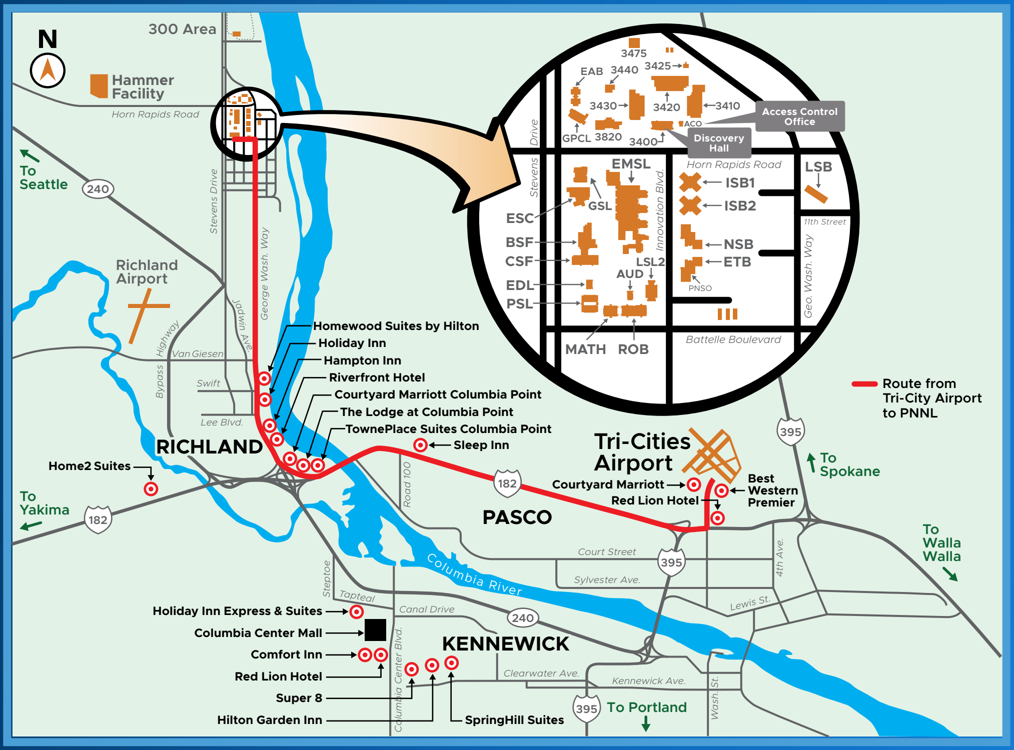

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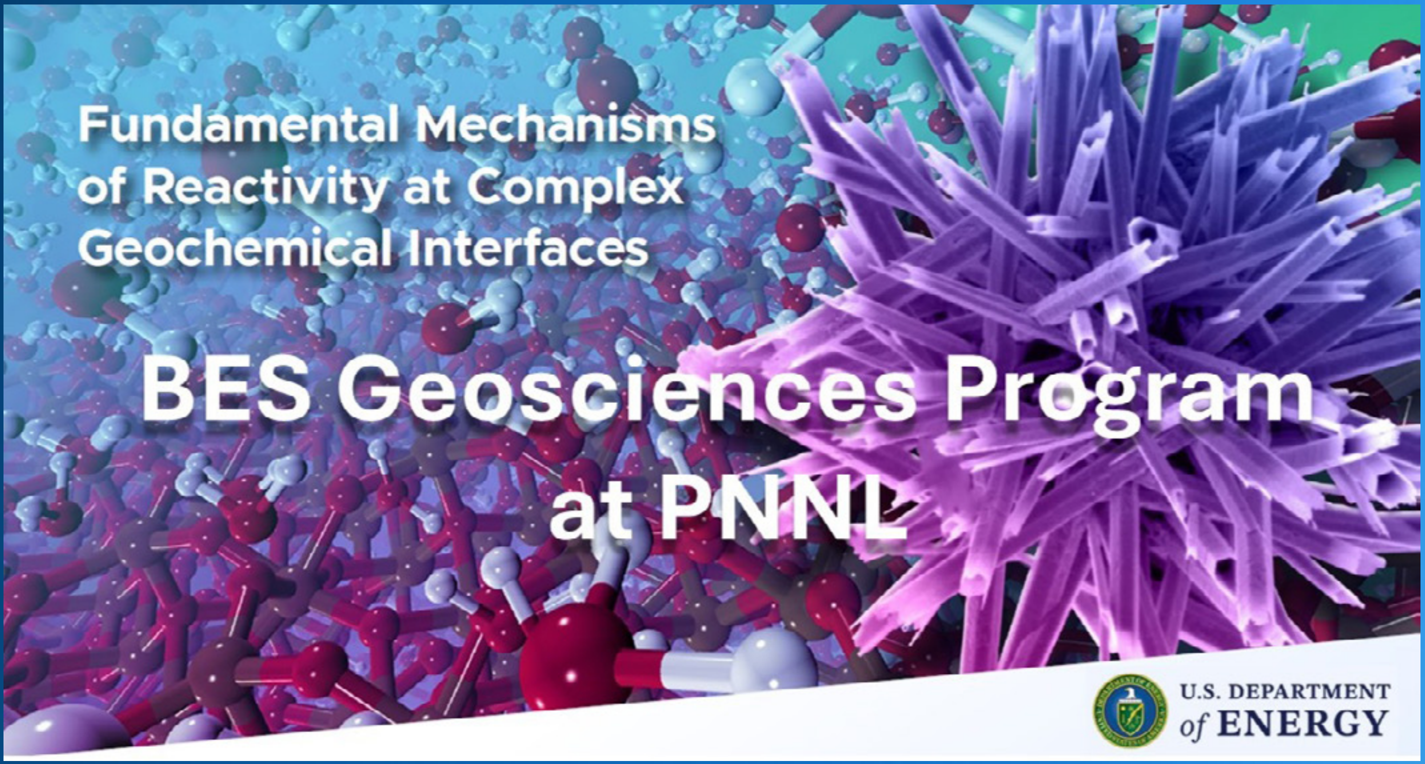

Fundamental Mechanisms of Reactivity at Complex Geochemical Interfaces

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