Caltech Student-Faculty Programs

Session N Abstracts

Applications of inverse theory to isotopic data in order to elucidate reaction dynamics: Principles and application to simple gas phase systems
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The structure and controlling variables (rate constants, etc.) of chemical reaction pathways are recorded in the measurable isotopic abundance ratios of network reactants, intermediates and products. Numerical modeling has shown that the combinatorics of isotopic substitutions in the reactions manifest themselves in distinctive clumped isotope signatures (i.e., proportions of multiply substituted isotopologues). Here we explore whether reaction network pathways can be inferred from measured isotopic abundance ratios by the application of mathematical inverse theory.

The use of inverse theory allows for the prediction of initial or prior conditions of a system from the observations of its output parameters. This application of inverse theory introduces an advance beyond previous, simpler approaches of forward modeling using pre-hypothesized reaction scenarios. However, such applications remain relatively limited. As an initial model system, we used inverse theory to model how all six isotopologues of hydrogen record information about the reaction network in which they participated them and how to access and use such information from experiments. First, we constructed a forward model for the chemical equilibrium and isotopic exchange of isotopologues of H_2 in gas phase, using a test reaction network of 24 reactions (with two different stoichiometries: H—H = H + H and H—H* + H—H = H—H + H—H*) and 9 unique species (H_2, HD, etc., and atomic H, D and T).

Taking advantage of the sparse stoichiometric matrices that describe the dynamics of such reaction systems, we apply several methods from inverse theory such as sparse system identification (SINDy) and inverse Jacobian methods to model different pathways through the reaction phase space corresponding to the addition or removal of certain reactions from the forward model simulating certain environmental conditions. For instance, in our model system described above we might wish to discriminate whether a system undergoes H2-H2 exchange, or H2 dissociation and reformation, or both. Our results demonstrate that inverse methods can identify different reaction pathways through chemical phase space, offering a method for determining possible reaction pathways from measured isotopic abundances of natural hydrogen. We are extending the application of these methods to more complex molecules systems containing H2, H_2O, CO_2 and/or methane, with the aim of using isotopic abundance ratios to inform the use of inverse theoretic models for predicting probable reaction pathways.

Constraining the lithification conditions for Martian regolith breccia using shock recovery experiments
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The meteorite Northwest Africa (NWA) 7034 and its paired stones are the only samples on Earth representative of the near-surface martian crust and are classified as a polymict breccia. Due to the variety of clast types and partial/full resetting of chronometric systems, the history of the meteorite is complicated, making it difficult to pinpoint a time and the conditions for lithification. Uniquely, NWA 7034 contains only crystalline plagioclase, rather than maskelynite, which defines a firm upper bound of < 20 GPa for the stone's shock pressure. We performed shock recovery experiments on martian regolith analog in order to constrain the pressure-temperature conditions for lithification without maskelynite formation. Analysis of recovered samples demonstrate that powdered basaltic analog can be lithified at a pressure of 6 +1/-3 GPa. The samples record partial preservation of plagioclase crystallinity and a transition from more crystalline plagioclase closer to the impact crater to increased maskelynite formation closer to the back wall of the recovery chamber, due to the reflected shock off the back wall to a higher pressure. We also tested a novel recovery chamber design with in situ pressure gauges, and additional test shot(s) will be carried out before use with another powdered rock sample. This work contributes to the overall understanding of NWA 7034's lithification timeline, broader impact processes, and the history of the martian near-surface environment.

Methane mosaics: Architecture of ANME-SRB mat aggregates
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Mentors: Victoria J. Orphan and Daniel Utter

Anaerobic oxidation of methane (AOM) occurs in microbial communities composed of anaerobic methanotrophic archaea (ANME) and their sulfur reducing bacterial partners (SRB) that together form syntrophic aggregates. These consortia are incredibly diverse in phylogenetic distribution and spatial structure, even forming 1-5 cm microbial mats, an invaluable structure to study the physiology and ecology of ANME. Recently, ANME-SRB mats were discovered and sampled at a methane seep off the coast of Santa Monica. However, the spatial and phylogenetic organization of these mats has remained largely uncharacterized. Therefore, we employed fluorescent in situ hybridization (FISH) and microscopy to visualize the spatial distribution of different ANME clades (e.g. ANME-2b, ANME-2c), SRB bacteria, and aggregates throughout the mat. We also used fluorescent stains targeting DNA, lipids, and glycoproteins to identify compositions of the extracellular matrices organizing individual aggregates into larger mat structures. Preliminary investigation revealed complexity and diversity of taxon arrangements and matrix materials beyond expectations of an organized structure. Image statistics and aggregate classification are expected to reveal distinct patterns that may inform future studies on these samples.

Pulse check: Biotic and abiotic drivers of the Birch effect
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Mentor: Woodward W. Fischer

Despite their pivotal importance in the global carbon budget, terrestrial carbon fluxes are poorly constrained and are sources of uncertainty in future climate projections. Despite containing the largest terrestrial reservoir of organic carbon, soil is a major contributor to such uncertainty, particularly in arid environments. In Mediterranean systems such as Southern California, moisture content varies dramatically throughout the year resulting in a high variability of the rate of organic matter remineralisation. It has been empirically demonstrated that there is a large pulse of CO_2 following rainfall events on such dry soils, known as the Birch effect. Various hypotheses have been postulated for the mechanisms behind the Birch effect, with previous studies suggesting that it is driven almost exclusively by biotic effects. In stark contrast, a suite of laboratory and field experiments highlight a transient abiotic pulse of CO_2 upon rainfall.

Wetting experiments on carbon free soil analogues demonstrate a near instantaneous increase in soil CO_2 concentration, which can only be driven by an abiotic response to simulated rainfall. The amplitude of this response is increased when the specific surface area is artificially raised, implying a crucial role of desorption of CO_2 from the surface of soil particles. When this is repeated with organic rich soil added, the amplitude and decay time of the pulse increases, due to the combined effects of greatly enhanced surface area and superimposed soil carbon remineralisation. Laboratory studies were complimented by field experiments on the Caltech campus and at the Jalama Canyon Ranch, Lombok. Together, the Birch effect is closer to being untangled; the combined influence of an instantaneous pulse of CO_2 rich gas from the soil coupled with a delayed increase in soil carbon remineralisation.

Understanding the cloud-aerosol interactions in stratocumulus clouds using the EDMF framework
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Mentors: Tapio Schneider, Akshay Sridhar, Anna B. Jaruga, Olivia Alcabes, and Sajjad Azimi

Marine stratocumulus clouds play an important role in regulating the Earth's climate because they provide a net cooling effect, but they have proven quite a challenge to represent correctly in climate models. From micron-scale aerosols to macro-scale turbulent and convective motion, they are governed by physics that operates across a broad range of scales. In an attempt to capture this complexity in CliMA's atmosphere model, ClimaAtmos, the 2-moment microphysics model (2M) is coupled with the Eddy Diffusivity Mass Flux (EDMF) scheme. The combined parameterizations should be able to represent the effects of turbulent mixing and transport, as well as the microphysics leading to rain formation. To evaluate the EDMF+2M coupled sub-grid-scale parameterization's ability to produce sensible stratocumulus clouds, the liquid-water-path (LWP) and number concentration (N) time evolution of perturbed stratocumulus-like initial conditions ensembles are compared against those produced by large eddy simulations (LES). The EDMF+2M's ability to replicate the same effects of cloud thinning due to entrainment & precipitation and cloud thickening due to radiative cooling observed in LES outputs will inform us on whether the EDMF+2M bulk scheme can adequately represent the dominant physics in stratocumulus clouds.

Examining the $\delta^{15}N$ composition of fungi and lichen amino acids
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Mentors: Julia Tejada and Mattia Tagliavento

Establishing the trophic positions of organisms is crucial for understanding ecosystem structure and species interactions. Recently, amino acid stable isotope analysis has emerged as a method for determining trophic position through comparing the isotopic value of "source" amino acids—those that experience little or no trophic fractionation and thus provide an internally referenced nitrogen baseline (e.g., phenylalanine)—to "trophic" amino acids—those that do fractionate when moving between trophic levels (e.g., glutamic acid). While some primary dietary sources, such as plants and algae, are isotopically well-characterized, others, namely fungi and lichens, remain understudied despite serving as key food sources and nutrient cyclers. Constraining their isotopic value is critical for accurate interpretations of the isotopic signals of their consumers and establishing a modern baseline for interpreting ancient ecosystems.

Here, we present $\delta^{15}N$ measurements of amino acids of mushrooms and lichen from Southern California. In addition to applying classic linear regressions, we performed unsupervised cluster analyses on our data, as well as our data in combination with published isotopic values for primary producers and consumers. We aim to get insights into trophic dynamics, nitrogen uptake, and metabolism among mushroom and lichen species.

Evaluating the ecological utility of bulk oxygen isotopes in western Amazonian mammal enamel
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Mentors: Julia Tejada and Joshua S. Anadu

Oxygen isotopes are often used to understand past climates, but the extent of their value in reconstructing ecological or physiological traits in mammals remains uncertain. This study analyzes bulk $\delta^{18}O$ in tooth enamel from 143 mammal specimens located in closed-canopy rainforests of western Amazonia. Samples encompass a range of diets and habitats across ten taxonomic orders. $\delta^{18}O$ values generally align with ecological expectations (e.g., aquatic species often have lower $\delta^{18}O$ than terrestrial species), but overlap among groups constrains their predictive utility in the absence of complementary data. Clustering analyses incorporating $\delta^{18}O$, $\delta^{13}C$, and $\delta^{15}N$ show that $\delta^{18}O$ contributes meaningfully to ecological grouping. To explore the drivers of $\delta^{18}O$ variation, a species-specific model was calibrated to Amazonian conditions and closely predicts the observed $\delta^{18}O$ values. Overall, while $\delta^{18}O$ holds limited power on its own, it can provide useful ecological insights when combined with additional data.

A quality mesh of the global ocean for simulations of the overturning circulation
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Mentors: Jörn Callies and Henry Peterson

Overturning circulation helps distribute heat and tracers around the globe, on thousand-year timescales. Recent observations and theory underline the importance of diabatic upwelling over sloping topography in shaping this circulation. Common numerical models use structured grids, which struggle to represent these new physical processes. To better simulate the overturning, an algorithm must be developed to generate a high-quality unstructured tetrahedral mesh of the oceans. In this project, we are building a pipeline for generating such a mesh using real bathymetry data and Gmsh meshing software. We determine closed coastline loops from the bathymetry, ensuring that the node spacing is consistent with the desired mesh resolution. The ocean bottom is then meshed with a varied horizontal resolution based on the local topographic slope. This, with the surface boundary, defines the three-dimesional ocean volume which is then meshed with tetrahedrons. We first applied this method to idealized basins in Cartesian space, verifying their quality using a finite element ocean model. We then extended the process to multiple realistic bodies of water, using the Marmara and the Black Seas as a test case. The next step is to generalize this algorithm to spherical geometry and, ultimately, create a global mesh of the ocean.

Modeling methane flux for long-term organic carbon sequestration
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Mentors: Alex L. Sessions and Madison Dunitz

One promising method for scalable carbon sequestration is industrial algal biomass farming in seawater. Evaporation of the sea water media increases the overall salt content for long term storage, reducing degradation and methane production. However, measuring the long-term emissions is a difficult task to do purely experimentally. Building on PFLOTRAN (a massively parallelized reactive-transport program) we model the relevant microbial reactions and molecular transport, to predict the flux of carbon dioxide and methane from the sequestered biomass. By modelling reactions such as acetoclastic methanogenesis, methylotrophic methanogenesis, and hydrogenotrophic methanogenesis, along with fermentation and acetogenesis, the model is able to forecast the net production and concentration of different chemical species on a 100-year timescale, to ultimately predict methane and carbon dioxide flux, beyond what we can experimentally test in a lab. The forecasted gas production from the model will be compared with future experimental data collected on samples on the order of weeks, months, and perhaps years.