Use of carbon and hydrogen stable isotopic composition to quantitatively assess natural gas generation

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The mechanisms of natural gas generation and migration are distinctly different from those that control oil accumulation, and consequently new tools and strategies must be developed in order to create effective gas exploration programs. Over the past few decades, carbon isotopic composition has been widely integrated with other geochemical tools in order to determine thermal maturity of gas, gas to gas, and gas to source correlation, as well as oil to oil and oil to source correlation. In recent years, interest has increased in the application of hydrogen isotopic composition of hydrocarbons to these essential questions of petroleum geochemistry. In this presentation, we will review the fundamental chemistry of kinetic and thermodynamic fractionations of both carbon and hydrogen stable isotopes in petroleum hydrocarbons affected by thermal alteration processes.

We have conducted an extensive number of pyrolysis experiments on a wide variety of different source rocks and whole oils in order to determine kinetic isotope fractionation constants for different hydrocarbon gas sources. However, without theoretical constraints on these fractionation constants, it is difficult to derive unique kinetic parameters based only on the laboratory simulation results. Consequently, we have performed a substantial number of *ab initio* quantum chemical calculations of kinetic isotope fractionations (both entropy and enthalpy terms) in order to developed a model for both carbon and hydrogen isotopes that, when coupled with compositional kinetics, allows for the prediction of the stable isotopic response to thermal stress, the gas quality (e.g., wetness), the thermal maturity of the gas source rock, and the gas to oil ratio (GOR).

We have also quantified the thermodynamic equilibrium fractionation constants for both carbon and hydrogen isotopes of methane based on *ab initio* quantum chemical calculations. Moreover, we have used a similar approach to determine the theoretical abundance of methane molecules containing both a heavy carbon atom (¹³C) and a deuterium atom. We will demonstrate that using the abundance of this doubly, isotopically substituted methane (¹³CDH₃), one might be able to predict the paleotemperature of methane generation. In order to measure the abundance of ¹³CDH₃, we have developed a new, laser-based, analytical technique and have obtained a detailed spectrum of synthetic ¹³CDH₃. When combined with traditional stable isotope modeling, this new approach will provide an additional dimension for understanding natural gas geochemistry.

Enhanced Uranium Sorption on Alumina through Surface Modification

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Sorption onto mineral surfaces is one of the principal mechanisms that governs the mobility and bioavailability of U(VI) in subsurface environments and in permeable reactive barriers. Although strongly dependent on pH and solution chemistry, U(VI) sorption is rather limited on some mineral and oxide surfaces. Consequently, sorption may not be effective in restricting its mobility. Considering that uranyl phosphates are highly insoluble and stable in geological settings, we explored mechanisms for increasing U(VI) sorption by pre-treating gamma-alumina surfaces with arsenate, which has a high affinity for binding with uranyl ions and is an analog for environmentally abundant phosphate.

Batch uptake experiments were conducted by treating gamma-alumina surface by pre-equilibration with arsenate, followed by addition of uranyl to the suspension at pH ~4. Parallel experiments were carried out with different U concentrations (from moderate to high) and corresponding particle loading and pretreated As concentrations. Results show a positive correlation between U(VI) uptake and [As]soln/[U]ini (defined as the ratio between As solution concentraion after pre-equilibration with alumina and the initial U concentration). Compared to ~20% U uptake on untreated gamma-alumina, U uptake by the pretreated gamma-alumina sharply increases to ~70% at [As]soln/[U]ini ~0.1 and ~100% at [As]soln/[U]ini >0.4, indicating the formation of ternary surface complex(es) and/or precipitates. X-ray absorption fine structure spectroscopy (XAFS) was applied at both the U L_{III}-edge and the As K-edge on selected sorption samples to characterize the local coordination environments of both elements and to identify the sorption products. XAFS fit results show U-As correlation at ~3.7 Å, suggesting the formation of U-As precipitates with a strucure similar to UO₂HAsO₄·4H₂O. U-U distances at ~3.9 Å and/or ~4.2 Å, likely corespond to formation of dimeric U species and/or schoepite-like uranyl oxy-hydroxide. The ratios between U-As precipitate and these uranyl dimer/oxyhydroxides are dependent on the [As]soln/[U]ini ratio and the absolute U initial concentration.

Results from this work can provide fundamental information for surface chemical processes in well-defined model systems as well as predictive information of U(VI) mobility in complex natural systems. Knowledge gained may also have applications for the selection and design of permeable reactive barriers, which can be used in removing dissolved uranyl from contaminated sites.