Enhanced *in situ* methanogenesis and microbial community analysis of coal beds

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Biogenic methane has enormous potential as a sustainable energy source and is found in a wide variety of subsurface, anaerobic, hydrocarbon bearing environments. The Powder River Basin in Wyoming, USA is an area previously shown to be an active 'geobioreactor', or an area where active *in situ* methanogenesis occurs as determined by coal conversion to methane in laboratory experiments, the presence of metabolic intermediates in coalbed methane formation waters, and the ability of the consortia present in these waters to convert the metabolites to methane. Understanding the composition and metabolism of the methanogenic consortia has been one of several key steps in commercializing the process of sustainable biogenic methane production.

In order to identify the microbes present in these methanogenic consortia, we performed microbial community analysis using error-correcting barcode pyrosequencing analyzed with the QIIME bioinformatic pipeline. This involved hundreds of samples collected from different locations within a set geographical area over several years. We used both bacterial and archaeal specific primers to amplify these distinct populations from our DNA samples. The QIIME pipeline was used for library demultiplexing, OTU picking, alignment, taxonomic identification, and statistical analysis of community structure using Unifrac. Spotfire was used for visualization of QIIME results with metadata from the formation.

Here we demonstrate the large scale areal and temporal sampling for community analysis of coalbed methane (CBM) wells within a discrete but large area of the Powder River Basin. Temporal consists of the baseline state, followed by a bio-stimulation phase (i.e. Restoration) and enhanced methane production phase. Under baseline conditions, we find distinct bacterial and archaeal populations that vary by coal, water chemistry, and time. Community profile signatures help determine the areas of greatest methanogenic potential and identify patterns of ground water recharge, water movement, and potential metabolic bottlenecks. Data will be presented showing increased gas production over pre-restoration decline curves, the period of enhanced methane production and the observed changes in the microbial community structure associated with enhanced gas generation.

An Exafs and *ab initio* study of aquated Cd^{2+} and chlorocadmium(II) complexes up to 300°C

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The hydrothermal transport and deposition chemistry of cadmium in the Earth's crust is still poorly known. X-ray absorption spectroscopy and quantum chemical calculations can provide fundmental insight on a molecular level into the formation/stability and hydration of the geochemically relevant Cd(II) complexes.

We have measured the EXAFS of aqueous cadmium nitrate, perchorate and chloride solutions up to 300°C and at the equilibrium saturated vapour pressure using an X-ray optical cell employing silica glass windows. In dilute nitrate solutions (($0.01m\ Cd\ (NO_3)_2/0.01m\ HNO_3$), Cd^{2+} is coordinated to 6 water molcules over the temperature range from 25 to 250°C. There is a small electrostrictive contraction of the Cd-water distance from 2.27 to 2.23Å with increasing temperature as the water solvent properties change at conditions along the two phase curve. In more concentrated nitrate and perchorate solutions (1.00m), the mono-, di- and trinitato- and monoperchoratocadmium (II) ion pairs were detected. The stepwise formation of chlorocadmium (II) complexes was also studied from 25 to 300°C in solutions having HCl concentrations from 0.001 to 3.00m. For example, in 3.00m HCl, the $CdCl_4^{2-}$ species predominated over the entire temperature range with the Cd-Cl distance remaining essentially constant at 2.46-2.45Å.

The computational part of the study was designed to provide further insight into the nature of Cd^{2+} hydration as well as to the coordination and hydration of the cadmium chloride complexes. We performed a systematic survey of the equilibrium geometries of $CdCl_m\ (H_2O)_n$ for m=0-4 and n=0-11. We employed the cc-pVnZ (PP) (n=D, T) correlation consistent basis set for Cd, cc-pV (d+n)Z (n=D, T) for Cl and cc-pVnZ (n=D, T) for H and O (abbreviated as VnZ (PP) (n=D, T). Geometry optimisations for the various hydrated complexes were performed at the RHF and the results thereof then applied as starting geometries for subsequent MP2 level calculations. In the case of $Cd\ (H_2O)_6^{2+}$ for example, the optimal Cd-O distance is 2.28Å. If 7 waters are constrained to the first shell, then the distance extends to 2.35Å, however, this geometry with $7H_2O$ is unstable.