

Improved carbon isotope modeling of biogenic coalbed methane systems: The nature of initial CO₂

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Carbon isotope signatures (e.g. $\alpha_{\text{CO}_2\text{-CH}_4} = (\delta^{13}\text{C}_{\text{CO}_2+1000})/(\delta^{13}\text{C}_{\text{CH}_4+1000})$) for distinguishing acetoclastic methanogenesis vs. CO₂ reduction were investigated in a biogenic coalbed methane (CBM) system, the Powder River Basin (WY/MT, USA). Past studies of this basin present inconsistent isotopic [1,2] and microbiological [3,4] evidence of methanogenic pathways.

Combined gas and groundwater analysis of monitoring and CBM production wells along a 25 km transect indicates several geochemical trends from shallow, basin-edge wells to deeper wells. Broadly, these basinward trends indicate: increasing pH (7.4-8.5), alkalinity (13-33 meq/kg), and temperature (11-28 °C); increasing $\delta^{13}\text{C}_{\text{CH}_4}$ (-78 to -56‰), $\delta^{13}\text{C}_{\text{CO}_2}$ (-24.7 to 4.7‰), and $\delta^{13}\text{C}_{\text{DIC}}$ (-11.0 to 16.2‰) values; increasing calcite saturation indices (-0.71 to 0.60); increasing $\delta^2\text{H}$ (-164 to -129‰) and $\delta^{18}\text{O}$ (-21.2 to -17.2‰) values; and decreasing apparent inputs of sulfate from shallow formations. Across this gradient of geochemical and isotopic conditions, *apparent* values of $\alpha_{\text{CO}_2\text{-CH}_4}$ are characteristic of CO₂ reduction (most 1.05-1.07). Given that $\delta^{13}\text{C}$ values of residual CO₂ are distinctively >0‰ in closed CO₂-reducing systems, inputs of DIC from microbial respiration (e.g. sulfate reduction) and/or carbonate dissolution would contribute isotopically depleted CO₂ to the reactant pool. This initial CO₂ is modified by methanogenesis. The lower $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ values observed in shallower, calcite-undersaturated waters are consistent with possible inputs of alternative electron acceptors (e.g. sulfate) from shallow units. Moreover, subsequent reduction of this CO₂ would represent an early stage of methanogenesis yielding depleted $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{CH}_4}$ relative to late-stage methanogenesis, in which more of the CO₂ pool has been reduced [2]. Thus, both the nature of initial CO₂ and the extent of reactant pool consumption can strongly influence observed $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{CH}_4}$.

The potential role of acetate remains undetermined. Low acetate concentrations basinwide (low μM range [3]) imply (1) a depleted acetate pool or (2) steady-state acetate production and consumption. Analysis of compound-specific and intramolecular C isotope ratios of acetate may elucidate acetate's role. The relative importance of methanogenic pathways has implications for understanding subsurface contributions to the C cycle and for the potential stimulation of sustainable gas production from CBM systems.

[1] Flores *et al.* (2008) *Int. J. Coal. Geol.* **76**, 52-75. [2] Bates *et al.* (2011) *Chem. Geol.* **284**, 45-61. [3] Ulrich & Bower (2008) *Int. J. Coal. Geol.* **76**, 25-33. [4] Green, Flanagan & Gilcrease (2008) *Int. J. Coal. Geol.* **76**, 34-45.

Chemical, Optical and Magnetic Susceptibility Characterization of Coal Fly Ash

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Abstract

Following the December 2008 rupture of a coal fly ash retaining pond at the Tennessee Valley Authority (TVA) Kingston Fossil Plant near Harriman, Tennessee, a comprehensive monitoring effort was initiated to evaluate the extent of ash deposition in the terrestrial and aquatic environments directly impacted by the release. The chemical characteristics of ash and impacted sediment samples were determined through analysis for a variety of metals using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and mercury using cold vapor atomic absorption spectroscopy (CVAA). In addition, polarized light microscopy (PLM) was utilized for the determination of percent ash of sediment samples. A comparison of the percent ash data to the metals and mercury concentrations revealed a strong correlation between ash content and concentration of some metals constituents (e.g., arsenic, strontium, and selenium). Other metals constituents (e.g., aluminum, boron, and iron) demonstrated weak or no correlation to ash content.

In addition to monitoring associated with the recovery effort, a research team from Appalachian State University evaluated the use of mass magnetic susceptibility (MS) as a potential indicator of ash content. MS was observed to correlate fairly well with ash content in the river bottom sediment samples; however, MS measurements showed a weaker correlation to some elements typically considered to be constituents of coal fly ash (e.g., selenium).

Conclusion

This paper evaluates the correlations among various analytical techniques and potential uses of alternate methods as a cost-savings measure for monitoring. PLM may be useful as an alternate method for estimating metals concentrations based on ash content. In addition, MS may be useful as an alternate analytical method for estimating ash content in bottom sediments in aquatic environments.