

## $\delta^{13}\text{C}$ of acetate in Powder River Basin coal bed waters: New application to methanogenic pathways in biogenic gas systems

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Established H and C isotope fingerprinting techniques [1] can lead to inconsistent interpretations for delineating the pathways of methanogenesis (acetoclastic methanogenesis vs.  $\text{CO}_2$  reduction) in biogenic natural gas reservoirs. Compound-specific carbon isotope analysis of acetate, yielded during biodegradation and a direct precursor of  $\text{CH}_4$  and  $\text{CO}_2$ , complements indirect approaches utilizing carbon isotopes of accumulated products. An important control on  $\delta^{13}\text{C}$ -acetate is the preferential routing of the  $^{12}\text{C}$ -bearing compound through methanogenesis, leaving the unreacted (residual) acetate  $^{13}\text{C}$ -enriched [2]. Therefore, compound-specific C isotopic composition can provide a direct record of acetate utilization by methanogens. This is useful for assessing the relative importance of acetoclastic methanogenesis and  $\text{CO}_2$  reduction.

$\delta^{13}\text{C}$ -acetate for Powder River Basin (PRB) coal bed waters was determined by sample preconcentration (original concentrations  $<20\ \mu\text{M}$ ) followed by headspace solid-phase microextraction and GC-IRMS. Along a 25-km sampling line from a shallow-basin edge environment to a deeper, basin-interior environment in the PRB,  $\delta^{13}\text{C}$ -acetate exhibits substantial variability (-34.3 to -15.1‰) that broadly parallels trends in  $\delta^{13}\text{C}$ - $\text{CH}_4$  and  $\delta^{13}\text{C}$ - $\text{CO}_2$  (-78.2 to -56.2‰ and -24.7 to 8.5‰, respectively). Along this line,  $\delta^{13}\text{C}$ - $\text{CH}_4$  and  $\delta^{13}\text{C}$ -acetate exhibit a linear relationship with slope of 1.04 and offset of  $\sim 40\%$  ( $R^2=0.71$ ).

The variation of  $\delta^{13}\text{C}$ -acetate is consistent with methanogens utilizing acetate. The large range of  $\delta^{13}\text{C}$ -acetate is consistent with higher overall favorability of methanogenesis at the basin interior, relative to less-fractionating processes such as sulfate reduction that are significant in the shallow, basin-edge environment. It should be noted that  $\delta^{13}\text{C}$ -acetate is an average of methyl and carboxyl carbon within acetate, whereas the methyl group is the expected methane precursor in the acetate molecule. Intramolecular isotope analysis would yield additional diagnostic information on acetate conversion to methane.

[1] Whiticar (1999) *Chem. Geol.* **161**, 291-314 [2] Blair and Carter (1992) *Geochim. Cosmochim. Acta* **56**, 1247-1258