

## Coal biodegradation pathways: Evidence from $\delta^{13}\text{C}$ of acetate

D. M. AKOB<sup>1</sup>, D. S. VINSON<sup>2\*</sup>, D. S. DUNLAP<sup>1</sup>,  
J. C. MCINTOSH<sup>1,3</sup>, W. H. OREM<sup>1</sup> AND N. E. BLAIR<sup>2</sup>

<sup>1</sup>U.S. Geological Survey, Reston, VA USA

<sup>2</sup>Northwestern University, Evanston, IL USA

(\*correspondence: david.vinson@northwestern.edu)

<sup>3</sup>University of Arizona, Tucson, AZ USA

To understand pathways of coal biodegradation yielding methane, we monitored acetate and methane concentrations and compound-specific carbon isotope ratios during laboratory incubations of coal from the northern Powder River Basin (PRB), Montana (USA). Microbial populations degrading the coal included native coal microbes with the WBC-2 methanogenic consortium added [1]. Results from triplicate batch incubations are reported as mean  $\pm 1\sigma$ . Acetate concentrations increased rapidly from days 12-34, then remained essentially unchanged through 263 days ( $4.3 \pm 0.5 \mu\text{mol acetate/g coal}$ ), at concentrations at least 10x higher than natural PRB coalbed methane (CBM) waters. Methane accumulated exponentially from days 20-34, with a total of  $0.20 \pm 0.02 \mu\text{mol CH}_4/\text{g coal}$  produced by 263 days. The limited conversion of acetate to methane suggests that acetoclastic methanogens were in low abundance or inhibited in the incubations. Efforts are underway to stimulate and monitor acetate conversion to methane.

On day 12 ( $0.52 \pm 0.05 \mu\text{mol acetate/g coal}$ ), the  $\delta^{13}\text{C}$  of acetate was  $-18.0 \pm 2.9\text{‰}$ , which is  $^{13}\text{C}$ -enriched relative to PRB coal ( $\sim -25\text{‰}$ ). On day 50 ( $4.01 \pm 0.10 \mu\text{mol acetate/g coal}$ ), acetate  $\delta^{13}\text{C}$  was  $-10.8 \pm 1.1\text{‰}$  and  $\delta^{13}\text{C}$  of headspace  $\text{CH}_4$  was  $-28.7 \pm 4.1\text{‰}$ . The methane  $\delta^{13}\text{C}$  value was more positive than natural PRB CBM ( $-83\text{‰}$  to  $-51\text{‰}$ ) [2,3]. The excess of acetate relative to methane, and also the large difference between incubation and PRB methane  $\delta^{13}\text{C}$  values, indicate that natural subsurface processes and/or rates were not reproduced with fidelity in laboratory incubations.

Although microbes, environmental conditions, and acetate concentrations differ in our experiments from natural PRB CBM waters, these results indicate that biodegradation of PRB coal can yield acetate. Also, the concurrent  $^{13}\text{C}$  enrichment within unreacted acetate during the production of methane is consistent with acetate being a methanogenic substrate. However, other, yet-to-be-identified fractionation mechanisms during acetate utilization cannot be ruled out.

[1] Jones *et al* (2008) *Int. J. Coal Geol.* **76**, 138-150 [2] Flores *et al* (2008) *Int. J. Coal Geol.* **76**, 52-75 [3] Bates *et al* (2011) *Chem. Geol.* **284**, 45-61