Acetate biogeochemistry of methanogenic coal beds and shales

D.S. Vinson[1,] J.C. McIntosh[2], A.M. Martini[3], T.H. Darrah[4], M.F. Kirk[5], D.M. Akob[6], and N.E. Blair[7]

[1]University of North Carolina at Charlotte, Charlotte, NC 28223 USA (*correspondence: dsvinson@uncc.edu)
[2]University of Arizona, Tucson, AZ 85721 USA
[3]Amherst College, Amherst, MA 01002 USA
[4]Ohio State University, Columbus, OH 43210 USA
[5]Kansas State University, Manhattan, KS 66506 USA
[6]U.S. Geological Survey, Reston, VA 20192 USA
[7]Northwestern University, Evanston, IL 60208 USA

The role of acetoclastic methanogenesis in coals and shales is uncertain, especially given the slow production of acetate, an intermediate and CH_4 precursor, from fossil C_{org}. We report preliminary acetate in water from 4 groups: (A) Powder River Basin (PRB) coal (acetate <20 μM of δ^{13}C -34.3 to -15.1‰); (B) Michigan Basin-Antrim Shale (acetate <20-630 μM of δ^{13}C -26.7 to -14.0‰); (C) Illinois Basin coal (acetate <20-150 μM of δ^{13}C -24.9 to -3.1‰); and (D) incubation of PRB coal (acetate 120-1300 μM of δ^{13}C -19.3 to -9.2‰). These basins exhibit variations of sulfate (e.g. <0.1-10.4 mM in A) and other factors including chloride (B-C) and thermal maturity (lowest in A and D).

Two apparent trends of acetate vs. δ^{13}C-acetate were observed: (I) Acetate <20 μM across a range of δ^{13}C-acetate (groups A and C?); and (II) More positive δ^{13}C-acetate at higher acetate concentrations (groups B, C?, and D).

More positive δ^{13}C-acetate is consistent with methanogenesis, which leaves residual acetate ^{13}C-enriched. Intriguingly, elevated δ^{13}C-acetate contradicts the expectation that H_2-trophic methanogenesis dominates systems fueled by fossil C_{org} [1]. The data record acetate production balanced by utilization by competing methanogens and non-methanogens (e.g. sulfate reducers). Trend I suggests competition for acetate between methanogens and non-methanogens, perhaps linked to variations in sulfate supply and all maintaining low acetate concentrations. Trend II is consistent with methanogens utilizing acetate more effectively when acetate concentrations are higher, due to higher acetate production and/or less competition from non-methanogens [2].

Overall, acetate-utilizing methanogens seem to be active in these systems. However, acetate in D exceeds A by >10x and D plots on trend II, unlike A. This inconsistency illustrates the challenge of replicating substrate availability in the laboratory.

[1] Golding *et al.* (2013) *Int. J. Coal Geol.* **120**, 24-40. [2] Blair and Carter (1992) *Geochim. Cosmochim. Acta* **56**, 1247-1258.