

## An unusual opportunity to document Pleistocene microbial methanogenesis in a Devonian black shale reservoir

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The Devonian Antrim Shale is an organic, naturally-fractured black shale in the Michigan Basin that serves as a source and reservoir for natural gas. Permeability in the Antrim Shale is controlled by a well-developed network of major, through-going vertical fractures. The dominant fractures are regional, with conjugate NE and NW sets measured in cores and outcrops across the study area. Fractures are open or partially sealed with calcite.

Economic methane deposits occur along an arcuate trend, parallel to the northern margin of the Michigan Basin. Best gas production is limited to shallow depths, in proximity to where the Antrim Shale subcrops below glacial drift.

Stable isotopic data on fracture cements from

outcrops and cores in the study area provide evidence of bacterial methanogenesis and methane oxidation in the Antrim Shale (Fig. 1). The  $\delta^{18}\text{O}$  values in both formation waters and calcite cements have a narrow range ( $-4$  to  $-12\text{‰}$  and  $21$  to  $27\text{‰}$  SMOW, respectively) and increase with depth in the basin. Most cements from outcrops and quarries have low  $\delta^{13}\text{C}$  values ( $-41$  to  $-15\text{‰}$  PDB) while most cements in cores have more positive  $\delta^{13}\text{C}$  values ( $15$  to  $31\text{‰}$  PDB). The highest  $\delta^{13}\text{C}$  values in fracture cements are near isotopic equilibrium with dissolved inorganic carbon in the present formation fluids, which have unusually high  $\delta^{13}\text{C}$  values ( $+24$  to  $+32\text{‰}$ ).

The unusually broad spectrum of  $\delta^{13}\text{C}$  values in fracture cements ( $+31$  to  $-41\text{‰}$  PDB) can be related to aerobic and anaerobic bacterial processes that have been ongoing within this shallow, unconventional reservoir. Calcite with high  $\delta^{13}\text{C}$  values record cementation as a minor byproduct during anaerobic bacterial methanogenesis due to elevated  $\text{HCO}_3^-$  concentrations. Cements with low  $\delta^{13}\text{C}$  values formed during periodic meteoric recharge into the reservoir when surface waters carrying aerobic bacteria mixed with formation waters; metabolizing methane and other higher chain hydrocarbons to yield  $\text{CO}_2$  and precipitation of calcite. Preliminary  $^{230}\text{Th}$  dating of cements from fractures in outcrop yield a corrected age of 275,000 to 350,000 ybp, placing formation during the Pleistocene. It is likely that repeated glacial advances exposed the Antrim Shale at the basin margin, enhanced meteoric recharge into the shallow part of the fractured reservoir, and initiated the latest episodes of bacterial methanogenesis and methanotrophic activity recorded in these fracture cements.

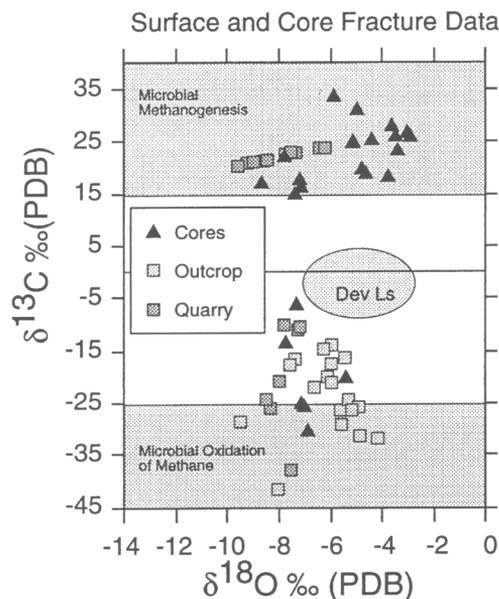


FIG. 1. Isotopic data from calcite cements.