Microbial production and modification of gases in sedimentary basins: constraints from isotopic compositions

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Unconventional natural gas reservoirs, such as organic-rich shales and coalbeds, are gaining in economic significance worldwide. Many of these fields contain some portion of microbial methane, either enhancing or replacing thermogenic gas. Importantly, these microbes produce isotopic and compositional effects on the various gas components that often obfuscate their origin. An expanding data set for gases produced from Devonian black shales in the Michigan and Illinois basins, USA, has allowed for a detailed examination of the related chemical and isotopic compositional changes in gas-water systems that trace these processes.

The Antrim Shale, within the northern margin of the Michigan Basin, has recently been shown to produce economic quantities of methane that is dominantly bacterial in origin, based on integrated chemical and isotopic analyses of formation waters and co-produced gas (Martini *et al.*, 1996). The most compelling evidence for microbial generation is the correlation between deuterium in methane and co-produced water (Fig. 1). Exploration for economic microbial gas deposits has been linked to low thermal maturity of the host rock organic matter, development of an open, permeable fracture network, and hydrologic conditions that permit freshwater recharge. Further expansion in the Michigan and Illinois basins has allowed us to develop this hypothesis in areas with differing geologic histories and hydrologic settings.

Expansion along the western and southern margins of the Michigan Basin at shallow depths within the Antrim Shale has yielded results that are very similar to those previously reported for the northern margin. Waters show evidence of meteoric influx (salinities increasing basinward from subcrop) and microbial activity. Gas chemistries suggest the occurrence of bacterial methanogenesis. In contrast, deeper, mid-basin Antrim Shale development has proven unsuccessful. Here, waters show no signs of meteoric mixing, having salinities and stable isotope compositions (O and H) typical of basinal brines. The gases produced include significant volumes of ethane and propane. Importantly, the correlation between the deuterium in methane and that in co-produced waters is absent. These results suggest the gas produced is thermogenic.

The isotopic effects of microbial activity are also seen in the $\delta^{13}C$ values of ethane. The $\delta^{13}C$ values for methane and ethane are plotted against the $\delta^{18}O$ values of co-produced waters in Fig. 2. The $\delta^{18}O$ values represent the influx of dilute waters, with the most negative values being from shallow wells near the subcrop of the shale, and the most positive values being from deeper wells within the basin. The methane values are invariant while those for ethane become increasingly higher as the $\delta^{18}O$ values of

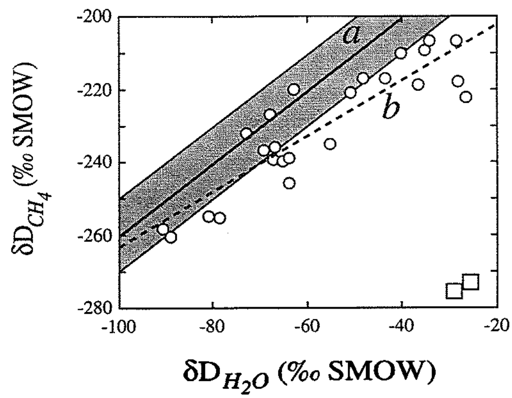

FIG. 1. Hydrogen isotope values of CH_4 and H_2O from paired Antrim Shale gases and formation waters. (a) A best fit line through the data (dashed line) and (b) the theoretically predicted microbial CO_2 reduction line (solid line) are shown (Schoell, 1980). Also shown are two deep mid-basin Antrim Shale wells (open squares).

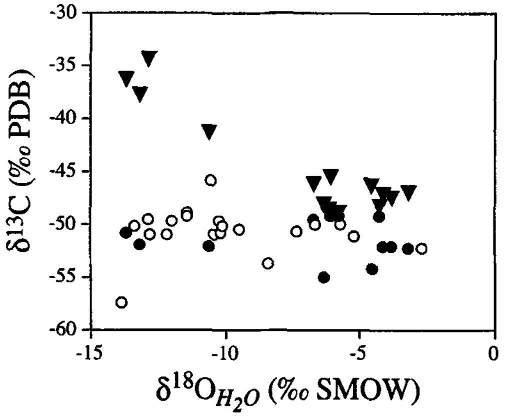

FIG. 2. Antrim Shale δC values for CH_4 (open circles) and C_2H_6 (filled triangles) versus δO values for co-produced H_2O. Paired ethane and methane values are shown as filled circles.

formation water decrease. This relation suggests the existence of some process affecting the isotopic composition of the ethane as the formation waters vary. Bacterial oxidation of ethane would permit these isotopic changes, which occur most dramatically near the subcrop where oxygenated meteoric waters have entered the Antrim Shale. This mechanism accounts not only for the shift in $\delta^{13}C$ values for ethane, but also for part of the geographic trend in gas composition as ethane and higher chain hydrocarbons are preferential removed.

The New Albany Shale, Illinois Basin, also has a well-developed fracture network and thermally immature organic matter. New exploration has allowed further hypothesis testing on the association of microbial gas with meteoric influx, in a setting with a more complex structural and hydrologic history. Co-produced waters reflect both meteoric and basinal brine sources, and a more complicated hydrologic model than that for the Antrim Shale emerges. Gas and water compositions indicate both microbial and thermogenic methane components, suggesting a potential mixed gas resource.

The results of these studies can be integrated into a predictive model for microbial gas exploration. Key geochemical indicators inhabit both the gas and co-produced water. A straightforward case is extremely high carbon isotope values for both the dissolved inorganic carbon in the water and co-produced CO_2 gas. In contrast, the $\delta^{13}C$ of methane is of limited use in these reservoirs as they fall between the commonly accepted field for thermogenic and microbial gas. Finally, where conditions allow, the $\delta D_{water}/\delta D_{methane}$ relations provide an excellent indicator of microbial contributions to the total methane content of the reservoir.

References

Martini, A.M., Budai, J.M., Walter, L.M., and Schoell, M. (1996) *Nature*, v. **383**, p. 155–7.

Schoell, M. (1980) *Geochim. Cosmochim. Acta*, **44**, 649–61.