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Research papers

Constraining the timing of microbial methane generation in an organic-rich shale using noble gases, Illinois Basin, USA

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ABSTRACT

At least 20% of the world's natural gas originates from methanogens subsisting on organic-rich coals and shales; however in-situ microbial methane production rates are unknown. Methanogens in the Upper Devonian New Albany Shale in the Illinois Basin extract hydrogen from low salinity formation water to form economic quantities of natural gas. Because of this association, constraining the source and timing of groundwater recharge will enable estimation of minimum in-situ metabolic rates. Thirty-four formation water and gas samples were analyzed for stable isotopes (oxygen and hydrogen), chloride, tritium, ^{14}C, and noble gases. Chloride and $\delta^{18}O$ spatial patterns reveal a plume of water with low salinity (0.7 to 2154 mM) and $\delta^{18}O$ values (−0.14 to −7.25‰) penetrating ~1 km depth into evapo-concentrated brines parallel to terminal moraines of the Laurentide Ice Sheet, suggesting glacial mediated recharge. However, isotopic mixing trends indicate that the recharge endmember (~−7‰ $\delta^{18}O$) is higher than the assumed bulk ice sheet value (<−15‰ $\delta^{18}O$), and similar to modern local precipitation (−7.5 to −4.5‰ $\delta^{18}O$). Continental paleoprecipitation records reveal that throughout the Pleistocene, $\delta^{18}O$ of precipitation in the region ranged from −10 to −5‰, suggesting that the dilute groundwater was primarily sourced from paleoprecipitation with minor contributions from glacial meltwater.

For the majority of samples the atmosphere derived ^4He contribution is negligible, and the ^4He is dominated by a crustal radiogenic source, with near complete transfer of dissolved noble gases to the gas phase. In addition, mantle derived helium is negligible for all samples (<1%). Helium-4 ages of formation waters associated with natural gas accumulations range from 0.082 to 1.2 Ma. Thermogenic methane is associated with older fluids (average 1.0 Ma), as compared to microbial methane (average 0.33 Ma), consistent with chloride and $\delta^{18}O$ data. However, all groundwater in the study area was influenced by Pleistocene recharge. Estimated in-situ microbial methane production rates range from 10 to 1000 TCF/Ma — ~10^4 to 10^6 times slower than average laboratory rates from coals. Findings from this study have implications for targeting undeveloped microbial gas accumulations, improving natural gas reservoir estimates, the potential of in-situ methanogen stimulation, and understanding biologic cycling of carbon in subsurface reservoirs.

1. Introduction

Methanogens have generated economic quantities of natural gas in subsurface organic-rich units such as coals and black shales. Currently this microbial methane supports at least 5% of United States' and Canada's energy needs (Rice, 1992; OEE, 2008; EIA, 2010), however little is known about the origins, residence times, and production rates of in-situ microbial communities (e.g. Schlegel et al., 2011). These knowledge gaps are critical in investigating the potential of in-situ methanogen stimulation and carbon cycling in biologically-active reservoirs.

In the Illinois Basin, economic reservoirs of microbial methane occur in the Upper Devonian New Albany Shale in association with anomalously low salinity formation water (McIntosh et al., 2002). A linear correlation between the δD values of the water and the co-produced methane demonstrates that methanogens extract hydrogen from the low salinity water to form methane (Schoell, 1980; Martini et al., 1998). The anomalously low salinity water extends from the basin margin to ~1 km depth in the shale and has a pattern divergent from simple infiltration from the basin margin subcrop (McIntosh et al., 2002). Rather, the orientation of the plume corresponds to Pleistocene ice lobes that advanced and retreated into the basin multiple times (Killey, 1998; McIntosh et al., 2002), suggesting glacial meltwater recharge from either subglacial recharge or proglacial

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lakes. However the $\delta^{18}O$ values associated with the dilute plume (−7.5 to +1.1‰) are not as low as would be expected for glacial recharge (<−15‰ $\delta^{18}O$), and mixing trends indicate a relatively high $\delta^{18}O$ value (~−7‰) for the freshwater endmember (McIntosh et al., 2002).

Isotopically-enriched recharge waters may have been sourced from: 1) modern precipitation (−11.0 to −4.5‰ $\delta^{18}O$), 2) a mixture of isotopically depleted Pleistocene-aged recharge and formational brines, or 3) an isotopically enriched Pleistocene aged source. This study constrains the source and timing of recharge in the New Albany Shale by comparing calculated ^{4}He groundwater ages derived from produced natural gas samples with stable isotopes (oxygen and hydrogen), chloride, tritium, and ^{14}C values from the produced water. This data set is enhanced by including published paleoclimate data for the Illinois Basin area. Results demonstrate that climate change can have profound effects on basin-scale groundwater recharge, driving freshwater recharge deep into sedimentary basins, which may also stimulate microbial methane generation in the relatively recent geologic past (<2 Ma), enabling the estimation of in-situ microbial methane production rates.

2. Geologic setting

The Illinois Basin, located in the midcontinent of the United States, is an interior sedimentary basin centered in southern Illinois (Fig. 1). The basin is oblong NW–SE, ~620 km long, ~375 km wide, over 4.5 km in depth, and filled with shallowly dipping (6 to 14 m/km) Paleozoic sediments (Zuppann et al., 1988). The basal sedimentary units are a thick sequence of Cambrian–Ordovician sandstones and carbonates overlying the Precambrian basement (Swann, 1968). Late Ordovician to Mississippian units are composed primarily of carbonates with interbedded sandstones and shales (Swann, 1968). Late Mississippian to Pennsylvanian units are generally comprised of interbedded shale, carbonates, and coal (Swann, 1968). Topping the sedimentary sequence are the surficial Quaternary glacial sediments that form the basin topography, with less than 300 m of relief (Swann, 1968; Zuppann et al., 1988). The basin is bounded to the north by the Kankakee Arch and Wisconsin Arch, to the east by the Cincinnati Arch, to the southwest by the Ozark Dome and Pascola Arch, and to the west by the Mississippi River Arch (Buschbach and Kolata, 1990). The Illinois Basin was deformed along its southern margin during the late Paleozoic through Mesozoic by tectonic uplift of the Pascola Arch and downwarping of the Mississippian Embayment (Buschbach and Kolata, 1990). The Cottage Grove and Rough Creek–Shawneetown Fault System, which trends east–west through the south-central basin, was active throughout the Paleozoic, and extends from the Precambrian basement to the surface (Buschbach and Kolata, 1990). Hydrocarbons in the basin are dominated by thermogenic processes in the deeper central portion of the basin in western Kentucky and southern Indiana, while microbial methane is predominant in Devonian shales and Pennsylvanian coals closer to the basin margins (Figs. 2 and 3) (McIntosh et al., 2002; Strąpoć et al., 2007).

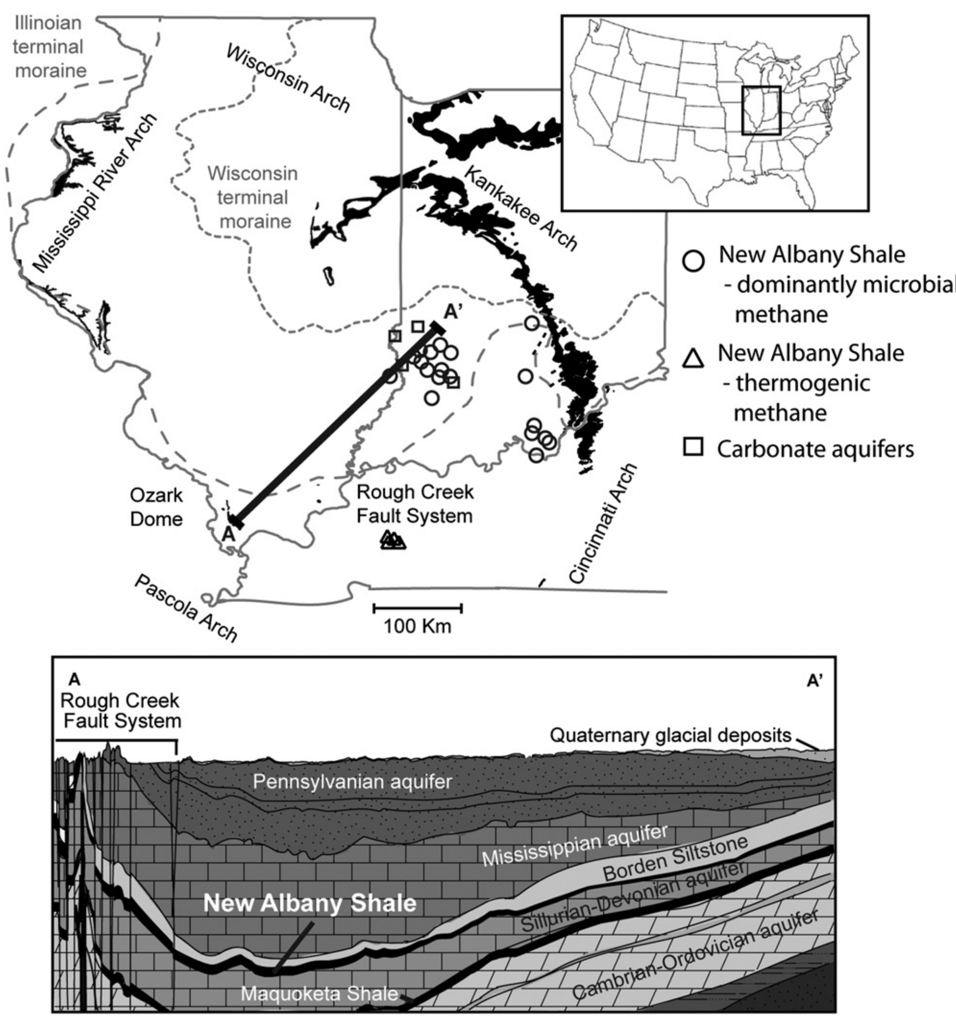

Fig. 1. Location map of the Illinois Basin, with New Albany Shale subcrop (black) and terminal moraines for Wisconsin and Illinoian glaciations (dotted lines). Also marked are major structural features and sample locations for this study. The cross-section through the Illinois Basin identifies important hydrologic units.