

## **Petrologic Evidence for Early Timing of Gas Generation in the Cretaceous Milk River Formation, Alberta and Saskatchewan**

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A detailed petrologic investigation of the Cretaceous Milk River Formation, southeastern Alberta and southwestern Saskatchewan, has been undertaken to determine the post-depositional alteration history of the unit as it bears on understanding the timing of generation of the large volume ( $>4 \times 10^{11} \text{ m}^3$ ) of contained biogenic gas. Petrography, scanning electron microscopy, X-ray diffraction, carbon and oxygen isotopic determinations, and fluid inclusion analyses were used to construct a temporal framework in which to place gas generation. This framework also serves to link methanogenesis to other events in the post-depositional history of the unit because the formation serves as both source of and reservoir for gas.

Of the numerous authigenic cements formed in the Milk River Formation, emphasis herein is on the carbonates because they are either volumetrically significant or they can be linked to methanogenesis. Siderite, one of the earliest authigenic minerals to precipitate, is present in sandstone and siltstone (volumetrically as much as 7%) as either small ( $<10 \mu\text{m}$ ) rhombic crystals in intergranular interstices or as moderate to large (up to  $50 \mu\text{m}$ ) overgrowths on detrital dolomite grains. In mudstone, however, the siderite occurs in large (up to 15 cm in height) concretionary masses as a mosaic of interlocking rhombic crystals (each  $\sim 5\text{-}7 \mu\text{m}$  across). In concretions,  $\delta^{13}\text{C}_{\text{PDB}}$  values for siderite range from  $-1.99$  to  $-14.23$  per mil (‰) and  $\delta^{18}\text{O}_{\text{PDB}}$  values range from  $-10.87$  to  $-19.41$ ‰. The  $\delta^{13}\text{C}$  values for Milk River siderite suggest it formed during biogenic methanogenesis. Calcite, which cements siderite, occurs as poikilotopic cement in sandstone and siltstone in volumes ranging from  $<1\%$  to  $28.7\%$ . The  $\delta^{13}\text{C}_{\text{PDB}}$  values for calcite range from  $-3.68$  to  $-14.02$  per mil and the  $\delta^{18}\text{O}_{\text{PDB}}$  ranges from  $-0.63$  to  $-13.16$  per mil. Overlap of calcite and siderite isotopic values suggests both minerals formed from isotopically similar pore fluids.

Analysis of volatile organic and inorganic species in submicroscopic fluid inclusions, via mass spectrometry using a specialized apparatus, indicates that methane as well as other volatile compounds usually associated with bacterial metabolic processes (e.g., CO<sub>2</sub>, acetic acid ± COS, CS<sub>2</sub>, and H<sub>2</sub>S), occur in inclusions in both siderite and calcite. The presence of these components in the inclusions implies that bacterial methanogenesis was concurrent with carbonate precipitation. The homogeneous composition and absence of observable microfracturing in siderite, determined by SEM semi-quantitative analysis and from petrographic examination and SEM compositional mapping, respectively, together suggest that the fluid inclusions are primary. However, direct evidence is lacking because the inclusions are submicroscopic.

The petrographic data point to formation of both siderite and calcite early in the post-depositional history of the Milk River Formation. Although the carbon isotopic composition of the siderite suggests its formation may have been related to methanogenesis, the presence of methanic fluid inclusions in siderite helps to link methanogenesis to the timing of siderite precipitation. Thus, gas generation was also an early, post-depositional event. Methanic fluid inclusions in post-siderite calcite imply that methanogenesis continued at least through the time of calcite precipitation.