P113-TU

THE IMPACT OF MIXING ON THE $\delta^{13}C$ COMPOSITIONS OF SHALE GASES AND THE USE OF THE NATURAL GAS PLOT

Serguey ARKADAKSKIY[1], Karlis MUEHLENBACHS[2] and Barbara TILLEY[2]

1. Isobrine Solutions Inc. 3060 RTF build. 8308 114 St. Edmonton, AB, T6G-2V2. Canada
2. 3-22a Earth Sciences Building, University of Alberta, Edmonton, Alberta, T6G 2E3, Canada,

The Cretaceous Colorado Group shales in the central parts of the Western Canada Sedimentary Basin (WCSB) reservoir a mixture of bacteriogenic CH_4 and incipient thermogenic gases. The shale gases leak along the bores of petroleum wells completed in the underlying Lower Cretaceous strata. Stable isotope data demonstrate that most thermogenic gases (C2+) are of very low maturities (< 0.5 $\%R_o$ eq.) and appear not impacted by mixing and microbial oxidation (Rowe and Muehlenbachs 1999).

Colorado shales contain type II and III kerogen of low maturity (< 0.4 to 0.8 $\%R_o$ eq.), and the $\delta^{13}C$ of the Total Organic Matter (TOM) in the shales varies from -22 to -30 ‰ (V-PDB; Buckley and Tyson, 2003). Values lower than -24 ‰ are confined to the type II kerogen bearing Second White Specs (SWS) Formation. These values mark a global positive ^{13}C excursion at the Cenomanian-Turonian boundary (Buckley and Tyson, 2003).

The Natural Gas Plot (NGP, Chung et al., 1988) has been used to estimate the type and relative maturity of the source rocks from the $\delta^{13}C$ composition of C_1-C_n. Low levels of thermal maturity had prevented the generation of liquid hydrocarbons in the Colorado shales, thus, rendering kerogen the principal source of natural gas. This along with the $\delta^{13}C_{TOM}$ data, provides an opportunity to critically evaluate the use of the NGP on a large subset of leaking gas samples collected from the central part of the WCSB.

Statistical treatment of the $\delta^{13}C$ of C_2-nC_4 gases from 123 leaking gas samples demonstrates that the average $^{13}C_{NGP\ intercept}$ value is -22.5 ± 6.7 ‰ with a mean R^2 of 0.91 ± 0.15. The high average value suggests that the bulk of the leaking gases originate from the SWS Formation. Predominant gas origin from the SWS is consistent with the lower activation energy threshold of Type II hydrogen-rich kerogen. This has resulted in an earlier onset of thermogenic gas generation in the SWS and, hence, production of larger quantities of natural gas at the low levels of thermal maturity in this part of the basin.

Although variability of the $^{13}C_{NGP\ intercept}$ values is the lowest amongst samples having $R^2 \geq 0.97$, a large number of those exhibit $\delta^{13}C_{NGP\ intercept}$ values lower than -22 ‰, with some as low as -7.5 ‰. An analysis of the concentrations and $\delta^{13}C$ compositions of those natural gas samples demonstrated that high $^{13}C_{NGP\ intercept}$ values likely result from mixing of natural

gases of different maturity (Figure 1). Mixing of two leaking gases in different proportions produces series of "hypothetical" gas mixtures with distinct $\delta^{13}C_{C2\text{-}nC4}$ compositions. When plotted on a NGP plot the $\delta^{13}C_{C2\text{-}nC4}$ values of those mixtures define series of regression lines with $\delta^{13}C_{NGP\ intercept}$ values ranging from -10.6 to -21.9 ‰ and R^2 values that vary from 0.97 to 1.0 (Figure 1). The two end member gas compositions shown on Figure 1 are not unique and attempts to "mix" other gases of similar concentrations and $\delta^{13}C_{C2\text{-}nC4}$ compositions produced similar results.

This study demonstrates that the thermogenic component of most Colorado shale gases from the central part of the WCSB was generated by a low temperature cracking of type II kerogen from the SWS Formation. It also demonstrates that a number of leaking gas samples having unrealistically high $^{13}C_{NGP\ intercept}$ values likely comprise mixtures of relatively immature gases with small amounts of more mature gases.

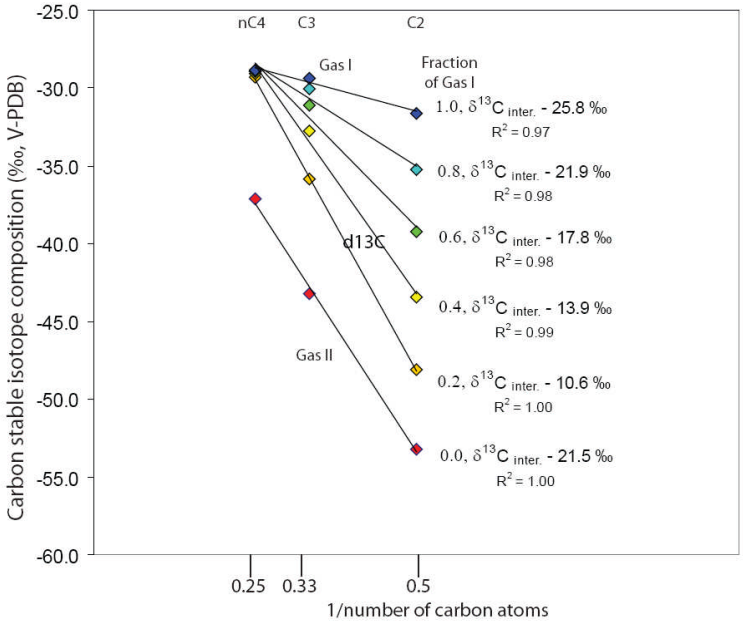

Figure 1. A natural gas plot with the $\delta^{13}C_{C2\text{-}nC4}$ of two end-member gases and their mixtures. The $\delta^{13}C$ compositions of C2-nC4 of gas I are -31.6, -29.3, and -28.9 ‰, while Gas II has $\delta^{13}C_{C2\text{-}nC4}$ of -53.2, -43.2 , and -37.1 ‰, respectively.

REFERENCES

Rowe, D., and Muehlenbachs, A. 1999. Low-temperature thermal generation of hydrocarbon gases in shallow shales. Nature (London) 398, 61-63.

Buckley, L. and Tyson, R.V. (2003): Organic facies analysis of the Cretaceous Lower and basal Upper Colorado Group (Cretaceous), Western Canada Sedimentary Basin – a preliminary report; in Summary of Investigations 2003, Volume 1, Saskatchewan Geological Survey, Sask. Industry Resources, Misc. Rep. 2003-4.1, CD-ROM, Paper A-10, 13p.