# Molecular and Isotope Effects during Production and Desorption of Unconventional Shale Gas and CBG

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## Summary

The stable carbon isotope ratios of hydrocarbon gases conducted on coalbed gas (CBG) production wells and canister desorption tests both demonstrate diagnostic changes that systematically vary with the degree of production and with desorption times. These shifts can provide decisive, predictive information on the behaviour and potential performance of CBG operations. Samples from producing CBG wells show a general depletion in $^{13}C$-methane with increasing production times and corresponding shifts in $\delta^{13}C$-$CH_4$ up to 35.8 ‰. Samples from canister desorption experiments show mostly enrichment in $^{13}C$ for methane with increasing desorption time and isotope shifts of up to 43.4 ‰. Also, $^{13}C$ depletion was observed in some samples with isotope shifts of up to 32.1 ‰. Overall, the magnitudes of the observed isotope shifts vary considerably between different sample sets, but also within samples from the same source. The $\delta^{13}C$-$CH_4$ values do not have the anticipated signatures of methane generated from coal. This indicates that secondary processes, including desorption and diffusion, can influence the values. It is also challenging to deconvolute these various secondary processes because their molecular and isotope effects can have similar directions and/or magnitudes. In some instances, significant alteration of CBG gases has to be considered as a combination of secondary alteration effects.

## Overview

The molecular and isotope composition of natural gases are widely used to characterize petroleum source rocks, reservoirs and the mechanisms of gas generation migration and accumulation. Changes to values in gas geochemical parameters, e.g., $C_1/C_{2+}$, $i$-$C_4/n$-$C_4$, $\delta^{13}C_1$, $\delta^{13}C_2$, $\delta^{13}C_3$, $\delta^{13}CO_2$, $\delta^2H$-$C_1$, $\delta^{34}S$-$H_2S$, etc., can be diagnostic for gas types and for processes including mixing, maturity and alteration (e.g., Schoell, 1988, Whiticar 1994). Although various suites parameters are generally successful as diagnostic tools, there are also situations that can confound reliable interpretation. These issues are often related to compositional shifts caused during gas movement, e.g., phase changes, desorption and diffusion. Such concerns were first suggested as early as 1954 by W.C. Gussow's paper on differential entrapment and they manifest themselves in several aspects.

Particular issues are the discussions surrounding the compositional discrepancy between reservoir gases and cuttings gases (e.g., Evans et al. 1971, Price and Schoell, 1995). The relative $C_{2+}$ hydrocarbon gas contents are typically much lower (drier) in reservoir or DST gases than the corresponding cuttings gases (wetter), e.g., the former could be ca. 85 % $CH_4$ ±15 % and latter ca. 20 % $CH_4$ ±10 %. Explanations (some conflicting) for this discrepancy range from mechanisms associated with source rock type, gas formation, maturation, phase separation and mixing, biodegradation, sorption, catalysts, etc., (e.g., Snowdon 2001, Mango, 2002, Snowdon, 2002, Abrams, 2005). Frequently, diffusional processes are proposed as the explanation in some situations (e.g., Antonov, 1968, Leythaeuser et al., 1980, Kross et al., 1988), as well as, evaporative fractionation (Thompson, 2010).

A further long-standing and inadequately resolved issue of interest is the potential for carbon isotope partitioning of gases, in particular methane, due to diffusional processes during migration, e.g., Colombo et al.

(1965), Galimov (1975), Fuex (1980), Prinzhofer and Pernaton (1997). This can active for short distance migration, e.g., leaky seals (permeability contrast), or possibly longer distance, especially for non-steady state conditions, e.g., Wang et al. (2015), Zhang and Krooss, (2001).

This paper presents empirical measurements of hydrocarbon gas molecular and stable isotope ratios on CBG deposits from:

1. Canister desorption time series experiments on samples collected from a suite of 7 CBG cores,
2. Time series measurements on production gas from a suite of 3 CBG wells.

In total, over 1000 gas samples from 10 sampling campaigns were obtained. Details of the collection and analyses are in Niemann (2006) and Niemann and Whiticar (2017). Some of the salient results to be discussed in the presentation are captured in Figures 1 - 3.
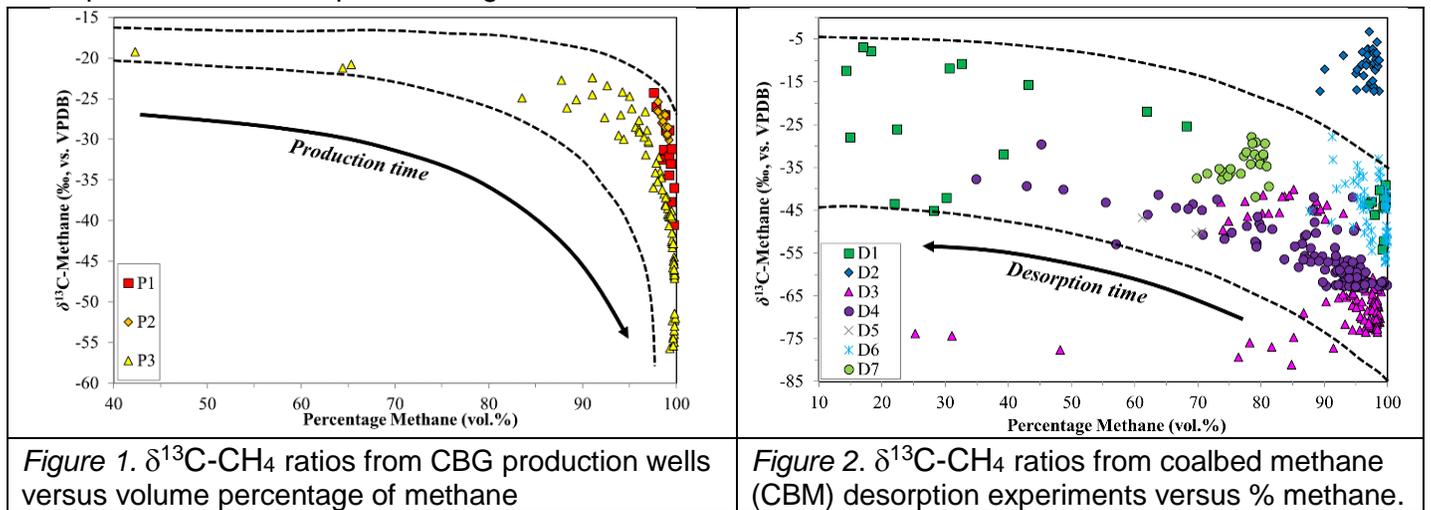


Figure 1. $\delta^{13}$C-CH$_4$ ratios from CBG production wells versus volume percentage of methane

Figure 2. $\delta^{13}$C-CH$_4$ ratios from coalbed methane (CBM) desorption experiments versus % methane.
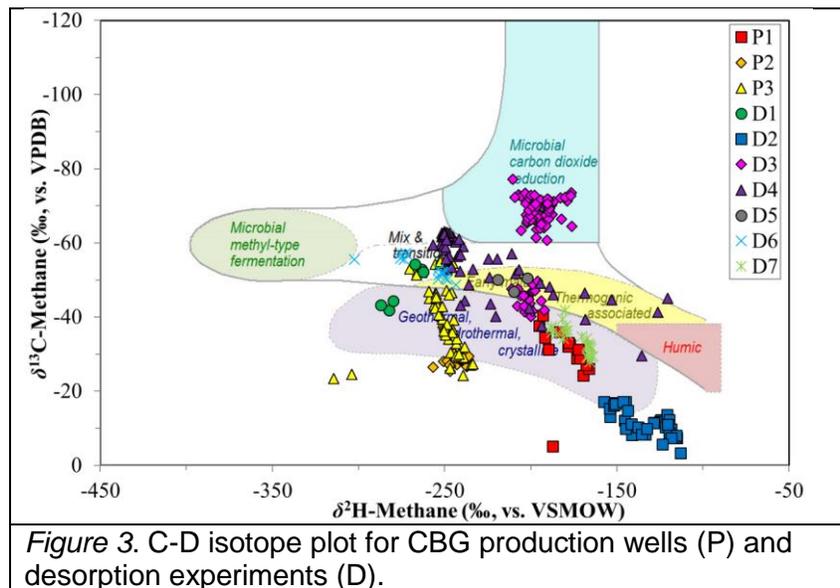


Figure 3. C-D isotope plot for CBG production wells (P) and desorption experiments (D).

## Conclusions

Interpretative challenges are due to the retentive capacity of coals, mixtures between gases of different origins (thermogenic, microbial) and mixtures of gases generated at different stages of the coalification process. Secondary processes, i.e., adsorption, desorption, mixing and diffusion can significantly alter the molecular and isotope composition of CBG gases.

CBG is most likely a mixture of gases generated from the coal at different times of the coalification process. This includes possible admixtures of primary and secondary microbial gas and, sometimes, gases generated from other coals and/or gases generated from different source rocks. The $\delta^{13}$C-CH$_4$ from desorption experiment and production samples show opposite trends with increasing desorption/production time. The methane from the former show $^{13}$C enrichment with increasing desorption time, while those from production show $^{13}$C depletion with increasing production time.

A schematic model is proposed to explain the observed isotope trend for CBG production samples of relative $^{13}$C enrichment for methane with increasing production time, indicating mixing of gases desorbing from different regions of an active coal seam during CBG production. Indications are found for sudden closure and correlating opening of fractures and fracture–systems in coal seams leading to desorption and consequently production of CBG from different sections of the coal or even from different intersected coal seams. With additional knowledge about the impact of secondary processes on the molecular and isotopic composition of CBG, the analyzes of stable carbon isotopes in CBG may provide further information about the total gas content of a given coal seam, including a more sophisticated estimation of lost and residual gas, residual gas, and may be therefore competitive to the currently used desorption canister approach.

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