Evolution of the Molecular and Stable Isotope Composition of Headspace Gas Desorbing From Drill Cuttings Collected in Sealed Jars

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Summary

The molecular and stable isotope composition (δ¹³C and δH) of low molecular weight (C₁-C₆) hydrocarbons (HC) are key parameters used to deduce the origin (i.e., thermogenic vs. bacterial) of natural gases. Two common sample types collected during drilling include (1) drill cuttings collected in sealed jars and (2) mud gas extracted from the drilling fluid and collected in gas cylinders. Gases desorbing from cuttings (headspace gas; HG) commonly exhibit greater molecular and stable isotopic variability compared to mud gas samples from the same interval. The widespread use of these sampling vessels and critical interpretations that are made based upon these data necessitate an investigation of the degree, and manner in which, the molecular and isotopic composition of HG varies over time.

Herein we document the evolution of the δ¹³C values (C₁-C₅) and molecular composition of 12 HG samples desorbing from Niobrara Formation drill cuttings over a period of five months. All of the HG samples show a rise in total HC (C₁-C₆) concentration, as well as progressive increase in CH₄ and attendant decrease in gas wetness (C₂+/C₁+) over time. Four of the five samples that initially had a thermogenic signature shift progressively towards more negative δ¹³C(CH₄) values over the course of the study (up to a -34‰ change). This behavior is consistent with secondary bacterial CH₄ production in the jars and suggests that the biocide (e.g., benzyalkonium chloride) that is normally added to these samples in the field may have been omitted.

The δ¹³C(CH₄) values and molecular composition of four of the seven samples that initially preserved a mixed microbial/thermogenic gas signature become progressively more negative and drier (>C₁/(C₂+C₃), respectively, over the first 3-4 weeks. For the remainder of the study, the same samples shift towards more positive δ¹³C(CH₄) values (up to a +32‰o change over the last four months of the study). The other three samples that initially exhibited a mixed microbial/thermogenic gas signature become progressively drier and show more positive δ¹³C(CH₄) values over the course of the entire study. This behavior is attributed to the combination of a secondary bacterial methane source in the jars and continued desorption of thermogenic/bacterial gas from the cuttings.

Accurate stable isotope and molecular composition data of HG are critical to the successful interpretation of the origin, maturity, and potential migration history of natural gases and associated liquids. This work demonstrates the importance of implementing standardized collection methods and timeframes for laboratory analyses, urges consistent use of a biocide, and provides a suite of parameters that can be used to assess the origin of secondary HC production in HG samples.

Introduction

Geochemical techniques are increasingly utilized to more fully understand and characterize components of unconventional petroleum systems. The molecular and stable isotope composition of low molecular weight hydrocarbons (methane-hexane; C₁-C₆) are critical parameters utilized to determine the origin and complex