



Clumped and conventional isotopes of natural gas reveal basin burial, denudation, and biodegradation history

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ABSTRACT

Formation and post-genetic alteration of hydrocarbons provide insights into the dynamic and complex geologic, hydrologic, and microbial history of shallow crustal environments. Clumped isotopologues of methane (e.g., $\Delta^{13}\text{CH}_3\text{D}$) have emerged as a proxy for constraining methane formation temperatures in sedimentary basins. However, unrealistically high apparent temperatures and microbial cycling of methane necessitate further investigation into how the generation and biodegradation of hydrocarbons may modify methane clumped isotopologue signatures. This study analyzed and modeled the clumped isotopologues of methane, in addition to traditional gas isotopes, to provide new insights into the origin, thermal maturity, migration, and biodegradation histories of hydrocarbons in the Paradox Basin in the Colorado Plateau. The basin was deeply buried in the geologic past and has been recently incised, leading to rapid denudation, enhanced meteoric circulation, and microbial activity. $\delta^{13}\text{C}_{\text{CH}_4}$ and $\text{CH}_4/\Sigma\text{C}_2+$ ratios suggest that most natural gases in various reservoirs throughout the basin are thermogenic in origin with variable thermal maturities. However, signatures suggestive of anaerobic oxidation of ethane and propane, and secondary microbial methane generation, exist. In the north-eastern part of the basin, $\Delta^{13}\text{CH}_3\text{D}$ values in reservoirs above and below the Paradox Formation source rocks are consistent with thermodynamic equilibrium, indicating that the thermally mature hydrocarbons equilibrated at $\geq 160^\circ\text{C}$ during maximum burial over 30–80 Ma. Disequilibrium $\Delta^{13}\text{CH}_3\text{D}$ values of natural gas in Paradox Formation reservoirs along the southwestern margin of the basin suggest the presence of low-maturity hydrocarbons consistent with the region's shallower burial history. Models of $\Delta^{13}\text{CH}_3\text{D}$ values based on the exchange rate of hydrogen isotopes between methane and water and the basin thermal history support that meteoric recharge and microbial activity, following incision/denudation over the past few million years, promoted anaerobic oxidation of hydrocarbons (particularly ethane and propane), biodegradation of crude oil, and generation of secondary microbial methane in shallow reservoirs.

1. Introduction

Understanding the evolution of hydrocarbons in sedimentary basins provides important insights into fluid generation and migration, and microbial activity (Martini et al., 1996; Head et al., 2003; Martini et al., 2008; Osborn and McIntosh, 2010). These processes are related to basin

burial and denudation history and play a key role in carbon cycling in the upper few kilometers of crust (Bose et al., 2013; Schweitzer et al., 2019). Molecular (C_1 , C_2 , C_3 , etc.) and isotopic (i.e., $\delta^{13}\text{C}$ and δD) compositions of hydrocarbons have been widely used as tracers of the origin of natural gas and post-genetic physical and biologic processes (Bernard et al., 1976; Chung et al., 1988; Prinzhofer and Huc, 1995;

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Prinzhofer and Pernaton, 1997; Schoell, 1988; Whiticar, 1999). However, these ‘traditional’ isotopic approaches often yield overlapping or ambiguous signatures of thermogenic versus microbial methane and biodegradation of hydrocarbons (Vinson et al., 2017). New techniques, based on measurements of multiply substituted (‘clumped’) methane isotopologues (Ma et al., 2008; Tsuji et al., 2012; Stolper et al., 2014a, b; Ono et al., 2014) may provide a more quantitative proxy to constrain temperatures of methane formation although fractionation may complicate the interpretation (Stolper et al., 2015; Wang et al., 2015; Douglas et al., 2016, 2017).

While many laboratory studies (Stolper et al., 2014b; Wang et al., 2016; Shuai et al., 2018; Xia and Gao, 2019) and well-constrained thermogenic gas fields (Wang et al., 2015; Douglas et al., 2017; Giunta et al., 2019) have yielded isotopologue equilibrium temperatures commensurate with temperatures of formation, many other complex basin systems with microbial gas have yielded more ambiguous results (Stolper et al., 2014a; Giunta et al., 2019). Isotopologues for thermogenic methane in the Potiguar Basin in Brazil show methane formation at deeper depths with higher temperatures compared to current reservoir conditions and provide new insights into gas migration and mixing associated with thermal and burial history (Stolper et al., 2014a). Natural gas in the Devonian Antrim Shale of the Michigan Basin is generated dominantly through microbial methanogenesis (Martini et al., 1998; 2003); however, methane isotopologue signatures suggest the natural gas is predominantly thermogenic in origin (Giunta et al., 2019), provoking questions about post-genetic reprocessing of methane isotopologues. Furthermore, several natural gas samples have been reported with anomalous clumped isotope values indicating unrealistically high apparent temperatures (>300 °C) of thermogenic methane formation (Douglas et al., 2017; Stolper et al., 2018; Xie et al., 2021), suggestive of kinetically controlled reactions. More conclusive interpretations of methane isotopologues require an understanding of the complex hydrologic and geologic (e.g., burial, uplift, tectonic activity) history of basins inducing different thermal regimes, fluid flow, and biodegradation of hydrocarbons, during and after their generation.

Post-genetic biodegradation processes in oil and gas reservoirs include biodegradation of crude oil producing secondary microbial methane (Matyasik et al., 2000; Pallasser, 2000; Masterson et al., 2001; Jones et al., 2008), anaerobic oxidation of methane (Knittel and Boetius, 2009; Valentine, 2011), and/or anaerobic oxidation of other short-chain hydrocarbons (James and Burns, 1984; Wenger et al., 2002; Martini et al., 1998, 2003, and 2008; Adams et al., 2013; Bose et al., 2013). The effects of post-genetic biodegradation on molecular and isotopic composition of hydrocarbons in natural gas have been evaluated using conventional isotopic approaches (Wang et al., 2005; Tilley and Muehlenbachs, 2006; Vandré et al., 2007; Zhou et al., 2008; Zhi et al., 2021; Jautzy et al., 2021), while the effects of biodegradation on clumped isotopologue compositions are still poorly defined (Wang et al., 2015, 2016).

The Paradox Basin in the Colorado Plateau contains widespread oil and gas fields and a dynamic geologic and hydrologic history (Nuccio and Condon, 1996; Rasmussen and Rasmussen, 2009; Whidden et al., 2014), providing a natural laboratory to study the co-evolution of formation water, hydrocarbons, and microbial communities over geologic time. Pervasive bleached, former redbed sandstones (e.g., Jurassic Navajo Sandstone) and residual bitumen provide evidence of large-scale (Beitler et al., 2003) hydrocarbon generation and expulsion during maximum burial, migration along faults into shallow sediments from the Pennsylvanian Paradox Formation source rocks, and subsequent post-genetic (microbial) alteration (Merin and Segal, 1989; Foxford et al., 1998; Chan et al., 2000; Thorson and MacIntyre, 2005; Hahn and Thorson, 2006; Hodson et al., 2016; Barton et al., 2018; Thorson, 2018; Kim et al., 2022a). Early-stage thermogenic gases may have also been post-genetically altered by high temperatures during maximum burial. Hydrocarbons may have been remobilized by topographically-driven groundwater flow and expelled or biodegraded by rapid incision and

breaching of shallow reservoirs (Beitler et al., 2003) following recent denudation of Colorado Plateau (<4–10 Ma; Lazear et al., 2013; Murray et al., 2016, 2019). Meteoric circulation around salt walls in the Paradox Basin generated high SO₄ from gypsum dissolution, enhancing bacterial sulfate reduction (BSR) in the presence of organic-rich shales (Kim et al., 2022a). BSR may have also been coupled with the anaerobic oxidation of hydrocarbons in reservoirs proximal to salt walls, as seen in previous studies of other environments, for example, ethane degradation coupled to BSR in sediments from hydrothermal vents (Adams et al., 2013), and BSR-coupled oxidation of alkanes, including methane, in marine hydrocarbon seeps (Bose et al., 2013). On the other hand, microbial methane, mixed with thermogenic gases, is present in Cretaceous coalbeds in east-central Utah (Mancos Shale/Ferron Sandstone; Rice, 2003) and Dakota Sandstone oil reservoirs in the Uinta Basin (Zhang et al., 2009), proximal to the Paradox Basin.

To better constrain the prolonged history of hydrocarbon generation and post-genetic (e.g., thermal and microbial) alterations in the Paradox Basin, we link the geological (e.g., erosion and incision) and hydrological (e.g., meteoric water circulation) history of the basin to natural gas geochemistry ($\delta^{13}\text{C}$, δD , $\text{CH}_4/\Sigma\text{C}_{2+}$, and $\Delta^{13}\text{CH}_3\text{D}$). We also evaluate the thermal equilibration of $\Delta^{13}\text{CH}_3\text{D}$ values using the rate of isotopologue exchange and thermal history of different parts of the basin. Results from this study extend the range of previously reported $\Delta^{13}\text{CH}_3\text{D}$ values and provide new insights into methane clumped isotopologues.

2. Study area

The Paradox Basin is located in southeastern Utah and southwestern Colorado, USA (Fig. 1A) within the Colorado Plateau. The basin is underlain by Precambrian basement rocks and was developed as a northeastward-deepening flexural basin in response to crustal loading by reverse faulting that generated the Late Paleozoic Uncompahgre uplift of the ancestral Rocky Mountains (Baars and Stevenson, 1982; Barbeau, 2003; Leary et al., 2017). The Late Devonian Elbert Formation, including the basal McCracken Sandstone member and a dolomite and shale upper member, was deposited in a shallow marine environment (Fig. 1B; McBride, 2016). Renewed transgression in the Mississippian initiated deposition of the Leadville Limestone (Fig. 1B; Nuccio and Condon, 1996). Subsidence along the northeastern side of the Paradox Basin and marine transgressions during the Pennsylvanian led to cyclical deposition of marine evaporites and interbedded black shales, forming the thick (1.8 km where the salt is not severely disturbed) Paradox Formation (Baars, 1966; Hite et al., 1984; Nuccio and Condon, 1996; Rasmussen and Rasmussen, 2009). In the southwestern part of the basin (e.g., Greater Aneth field), the Paradox Formation is dominated by shelf carbonates, including algal-mound buildups (Nuccio and Condon, 1996). The black shale interbeds of the Ismay and Desert Creek members (interval of the Upper Paradox Formation and the Cane Creek shale member of the Middle Paradox Formation) are major hydrocarbon source rocks (Figs. 1B, 2A, and 2B). The black shales contain up to 11–20% total organic carbon of a combination of Type II and Type III kerogen (Nuccio and Condon, 1996; Rasmussen and Rasmussen, 2009; Whidden et al., 2014). The amount of Type III kerogen, which is typically terrestrial organic matter, increases eastward toward the ancestral Uncompahgre Uplift (Nuccio and Condon, 1996).

Above the Paradox Formation, the Pennsylvanian Lower Honaker Trail Formation consists of limestone, sandstone, and shale deposited in a cyclic pattern from evaporitic to normal marine conditions. The Upper Honaker Trail Formation and overlying Permian Cutler Group are composed of arkosic sandstone sourced from erosion of the Uncompahgre Uplift. Triassic and Jurassic formations are composed of eolian and fluvial sediments with volcanic ash (Fig. 1B). The early Cretaceous sediments are composed of conglomeratic sandstone and mudstone (Nuccio and Condon, 1996), while the Upper Cretaceous Mancos Shale was deposited in the Western Interior Cretaceous seaway (Fig. 1B). Intrusion of laccoliths during the Paleogene and Neogene (28 ± 1 Ma)

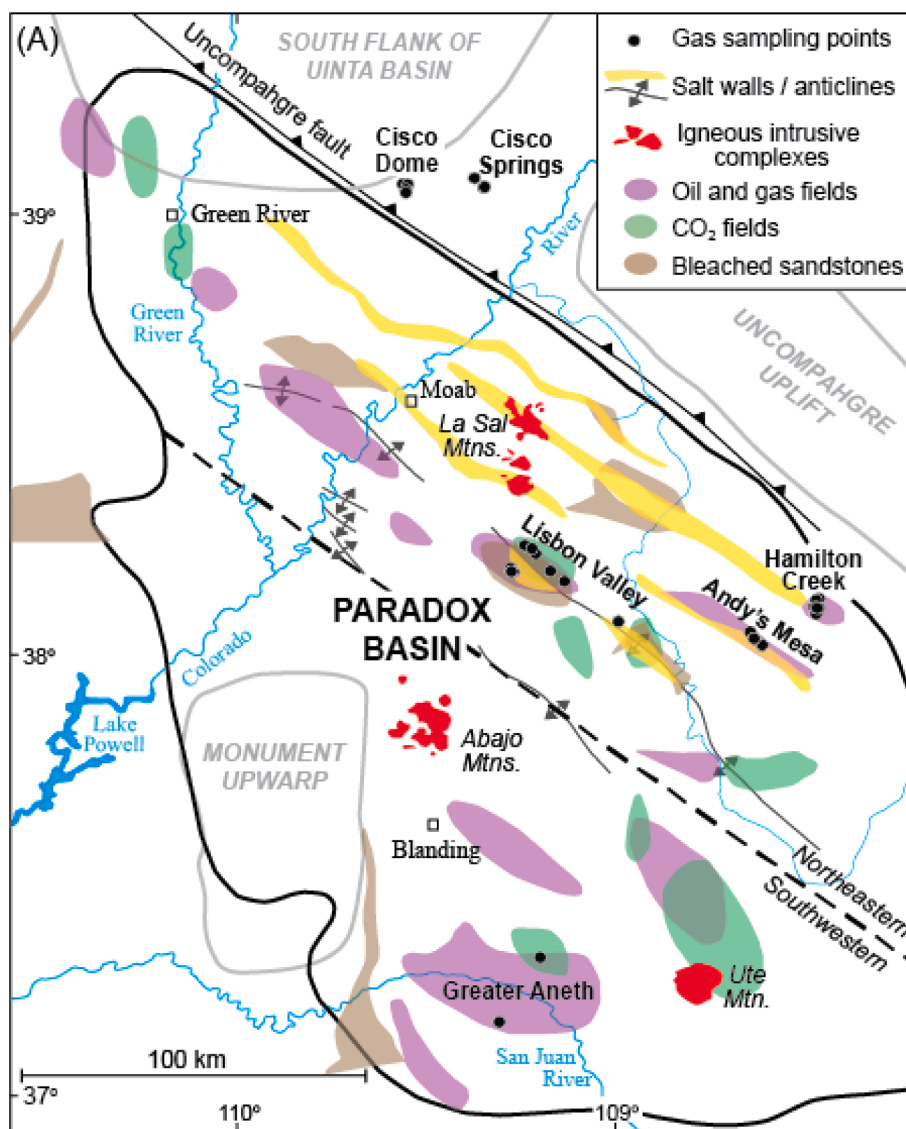


Fig. 1. (A) Location of the Paradox Basin, Colorado Plateau, USA, and spatial distributions of salt walls and anticlines, oil and gas fields, CO₂ fields, bleached sandstones, modified from Barton et al. (2018). Dashed line represents the basin extent. (B) Stratigraphic column of Devonian through Cretaceous formations with vertical distribution of bleached sandstones, organic carbon sources, and oil and gas reservoirs in different fields where gas samples were collected. Different sample symbols are shown in brackets. Vitrinite reflectance (R_o) values and corresponding oil and gas windows of the Upper and Middle Paradox Formation source rocks in northeastern/southwestern side of the Paradox Basin (Rasmussen and Rasmussen, 2009).

formed the La Sal, Abajo, and Ute mountains in the Paradox Basin (Fig. 1A; Nuccio and Condon, 1996; Friedman and Huffman, 1998; Barton et al., 2018; Murray et al., 2019).

Thick deposition of Permian through Neogene sediments led to plastic flow of the underlying Paradox Formation evaporites and created the salt walls/anticlines, associated faults (Hartley and Evenstar, 2018), and sub-basins along the northeastern side of the basin, for example in the Lisbon Valley areas (Cater and Craig, 1970; Doelling et al., 1988; Lawton et al., 2015; Nuccio and Condon, 1996; Trudgill, 2011). During the late Miocene, incision of the Colorado River and rapid denudation of the Colorado Plateau (<4–6 Ma, Murray et al., 2016 and 2019; <10 Ma, Lazear et al., 2013) removed most of the Cretaceous and overlying sediments (e.g., Mancos Shale confining units) (Nuccio and Condon, 1996), created relatively high topographic gradients (Karlstrom et al., 2012; Lazear et al., 2013; Pederson et al., 2013), and brought deep geologic formations and their fluids closer to the surface. The high topographic gradients allowed widespread paleofluid flow events resulting in ore mineralization (Bailey et al., 2022a and 2022b) and deep

meteoric circulation that flushed residual saline fluids from aquifers above and below the evaporite units and regenerated salinity and high SO₄ concentrations via dissolution of halite and gypsum (Kim et al., 2022a).

The Pennsylvanian Paradox Formation and overlying Lower Honaker Trail Formation comprise the middle hydrostratigraphic unit – a regional confining unit (Thackston et al., 1981; Hanshaw and Hill, 1969). Regional groundwater flow in the Pennsylvanian Upper Honaker Trail Formation through Cretaceous formations above the evaporites is mainly controlled by topography (the upper hydrostratigraphic unit) with recharge around salt anticlines, uplifts, and mountains (Hanshaw and Hill, 1969; King et al., 2014; Thackston et al., 1981). Mississippian through Devonian formations are considered as a single, lower hydrostratigraphic unit with a regionally extensive flow system toward the southwest, as well as with a locally recharged flow system around lacoliths, such as the Abajo and La Sal Mountains (Nuccio and Condon, 1996; Barton et al., 2018) or along the margins of the salt anticlines (Hanshaw and Hill, 1969; Thackston et al., 1981).

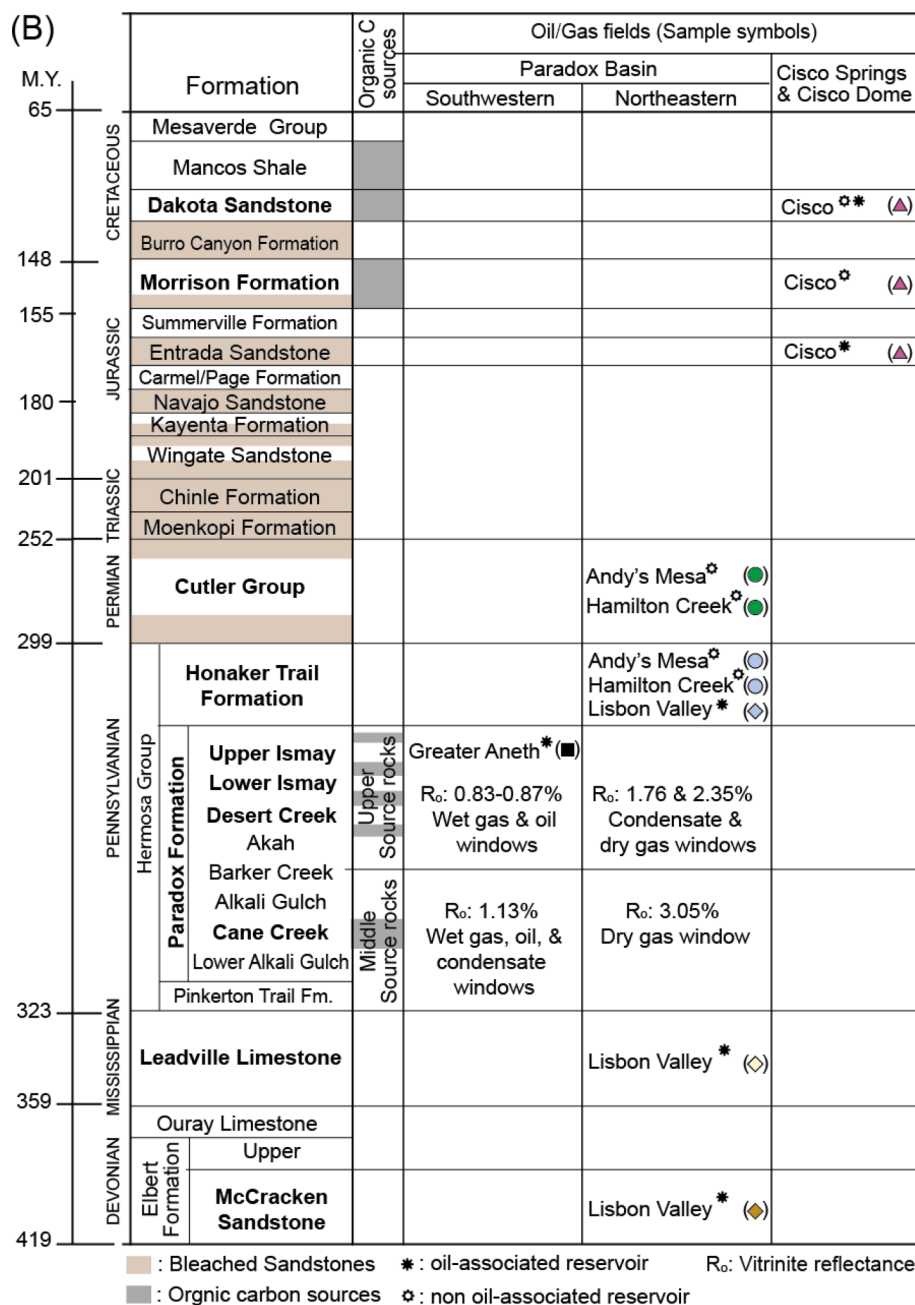


Fig. 1. (continued).

The relatively thick sedimentary sequence in the northeastern part of basin proximal to the Uncompahgre Uplift (e.g., Lisbon Valley and Andy's Mesa fields; Fig. 1A) resulted in deeper burial and higher thermal maturities of the Cane Creek source rocks in the Paradox Formation (Figs. 1B and 2A), compared to the south-central and southwestern parts of the basin (e.g., Greater Aneth field; Figs. 1B and 2B) (Nuccio and Condon, 1996; Rasmussen and Rasmussen, 2009). For example, in the Lisbon Valley, early generation of hydrocarbons in the Cane Creek source rocks of the Middle Paradox Formation began as early as ~156 Ma. Significant generation of hydrocarbons occurred ~84–100 Ma and continued until the source rocks reached a maximum burial depth of 6.6 km~25 Ma (Fig. 2A; Nuccio and Condon, 1996). Thermal maturities of the Cane Creek source rocks in the northeastern part of the basin are relatively high (3.05% R_o, vitrinite reflectance) within the dry gas window with ≥90% of transformation of kerogen (Fig. 1B; Rasmussen and Rasmussen, 2009). On the other hand, in the southwestern part of

the Paradox Basin, the Ismay-Desert Creek source rocks began early generation of hydrocarbons ~74 Ma, started significant generation ~45 Ma, and were buried at a maximum depth of 4.1 km~25 Ma (Fig. 2B; Nuccio and Condon, 1996). Current thermal maturities of the Ismay-Desert Creek source rocks in the southwestern part of the basin range from 0.87 to 0.83% R_o, within the wet gas and oil window with 46–54% transformation of kerogen (Fig. 1B; Rasmussen and Rasmussen, 2009). Significant oil and gas generation across the basin led to two peak upward and lateral fluid (i.e., water, oil, and gas) migration events around 66–100 Ma and 255–275 Ma (Lucero et al., 2020). Fluids generated within the source rocks likely migrated laterally within the Paradox Formation and vertically upwards along salt wall-bounding faults, especially in the northeastern part of the basin, and formed shallow reservoirs, for example in the overlying Honaker Trail Formation and Cutler Group in the Lisbon Valley, Andy's Mesa, and Hamilton Creek fields. Generation and primary migration of oil and gas from the Paradox

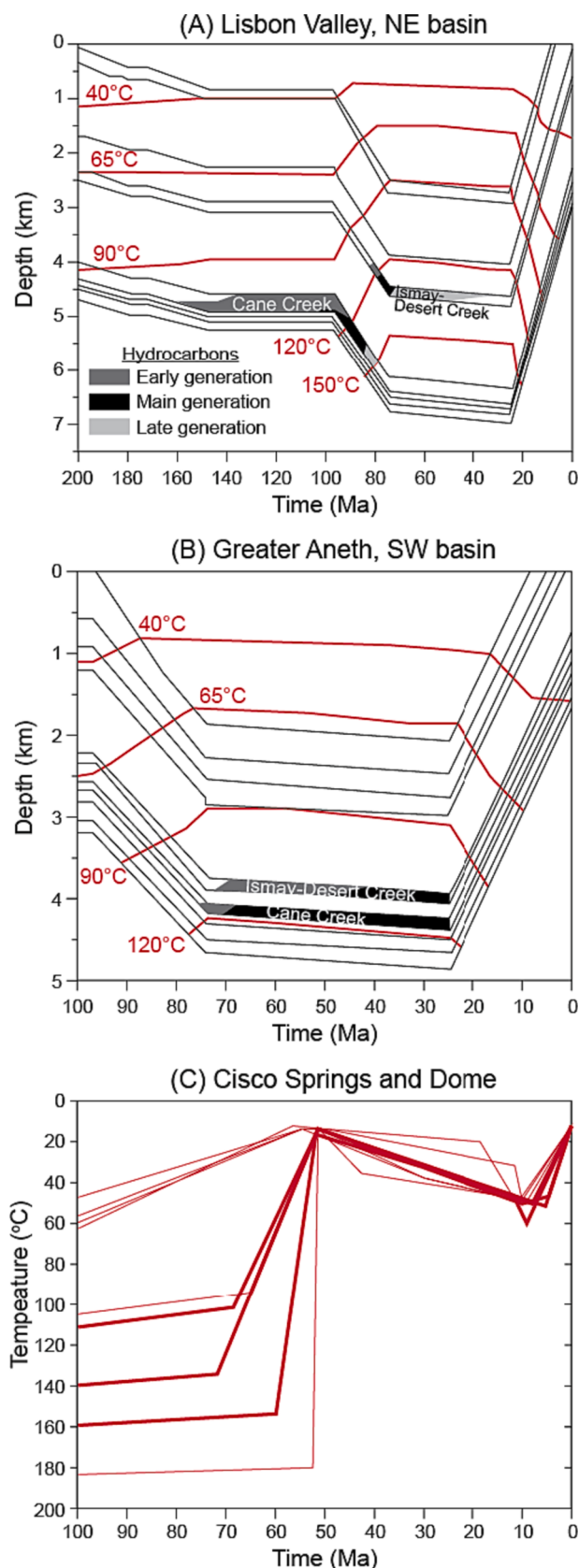


Fig. 2. Burial, thermal, and hydrocarbon generation history of (A) the Lisbon Valley field in the northeastern side of the Paradox Basin, (B) Greater Aneth field near the Monument upwarp in the southwestern side of the basin (modified from Nuccio and Condon, 1996), and (C) Cisco Springs and Dome field near the Hay Canyon area of Book Cliffs (modified from Hoffman, 2009).

Formation ceased near the end of the Miocene, as the basin was incised, eroded, and cooled, beginning <10 Ma (Lazear et al., 2013) or <4 –6 Ma (Murray et al., 2016; Murray et al., 2019).

The Cisco Springs and Cisco Dome fields (hereafter ‘Cisco field’) are located between the northeastern part of the Paradox Basin and the southern flank of the Uinta Basin (Fig. 1A), bounded to the north by the Mancos Shale outcrops in the Book Cliffs (Walton, 1956). The Cisco field lies upon north-west trending anticlines, which are a northern extension of the Uncompahgre Uplift (Walton, 1956; Hendel, 1961), that were formed by post-Cretaceous uplift of the upthrown block of the Uncompahgre fault (Young, 1983). In this region, Jurassic sediments unconformably overlie Precambrian rocks of the Uncompahgre Uplift (Young, 1983; Smouse 1996). Oil and gas in the Cisco field are dominantly produced from the Cretaceous Dakota Sandstone, with some production from the Jurassic Morrison and Entrada formations (Young, 1983) (Fig. 1). Different source rocks for hydrocarbons in the Cisco field have been hypothesized, including black shales in the Paradox Formation (Young, 1983) and/or organic-rich carbonaceous materials within the Morrison Formation, Dakota Sandstone, and/or overlying Mancos Shale (Hendel, 1961). The Mancos Shale and underlying sediments (e.g., Dakota Sandstone) reached ~ 110 to 190 °C during maximum burial ~ 100 Ma and experienced two rapid uplift/denudation events around 50–70 Ma and 10 Ma (Fig. 2C) (Hoffman, 2009), bringing the reservoirs closer to the surface under cooler conditions (20–60 °C) conducive for microbial degradation of hydrocarbons (McIntosh et al., 2023).

3. Methods

Thirty-three natural gas samples were collected from active oil and gas wells (Fig. 1A and 1B) producing from the: 1) Mississippian Leadville Limestone and/or Devonian McCracken Sandstone in the Lisbon Valley field; 2) Pennsylvanian Paradox Formation (Ismay-Desert Creek members) in the Greater Aneth field; 3) Pennsylvanian Honaker Trail Formation in the Lisbon Valley field; 4) Pennsylvanian Honaker Trail Formation or Permian Cutler Group in the Andy’s Mesa and Hamilton Creek fields; and 5) Cretaceous Dakota Sandstone and Jurassic Morrison (and Entrada) formations in the Cisco field (Fig. 1B and Table 1). Natural gas samples were collected in duplicate at the wellheads using a gas sampling manifold and Isotubes provided by Isotech Laboratories according to their instructions.

Natural gas samples were analyzed at Isotech Laboratories for gas composition and $\delta^{13}\text{C}$ and δD values of methane (CH_4) and higher chain hydrocarbons (C_2 – C_5). Molecular and isotopic ($\delta^{13}\text{C}$) compositions of CO_2 were also analyzed at Isotech Laboratories. Gas molecular composition (He , H_2 , Ar , O_2 , CO_2 , N_2 , CO , CH_4 , and C_2 – C_5) was determined on a Shimadzu 2010 Gas Chromatograph equipped with thermal conductivity and flame ionization detectors. The $\delta^{13}\text{C}$ and δD values of hydrocarbons for most of the gas samples and $\delta^{13}\text{C}$ values of CO_2 were determined by conventional offline methods consisting of chromatographic separation followed by combustion and dual-inlet isotope ratio mass spectrometry with a precision of $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 2.0\text{‰}$ for δD . δD values of ethane and propane and/or n-butane of eleven samples (asterisk marked in Table 2) were measured online via compound-specific analysis with gas chromatography combustion/pyrolysis isotope ratio mass spectrometry (GC-C/P-IRMS) (precision, $\pm 0.3\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 5.0\text{‰}$ for δD) due to low concentrations. All gas component $\delta^{13}\text{C}$ values are reported on a scale defined by a two-point calibration of LSVEC and NBS 19. Additional molecular and isotopic data from the Honaker Trail Formation (FF-4-20; MM36-14) from an unpublished dataset of Paradox Resources supplemented gas data for the Honaker Trail Formation (Tables 1 and 2).

Twenty-eight of the natural gas samples were also analyzed for the abundance of four isotopologues of methane ($^{12}\text{CH}_4$, $^{13}\text{CH}_4$, $^{12}\text{CH}_3\text{D}$, and $^{13}\text{CH}_3\text{D}$) using Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS) at the Massachusetts Institute of Technology (Ono et al., 2014). Methane was purified using an automated preparative GC system

Table 1

Sample location, depth, well type, and gas composition (mol%) of natural gases in the Paradox Basin.

Sample/well ID	Latitude	Longitude	Elevation (m)	Depth (m)	Field	Well	Formation	He	H ₂	Ar	O ₂	CO ₂	N ₂	CO	CH ₄	C ₂	C ₂ H ₄	C ₃	C ₃ H ₆	iC ₄	nC ₄	iC ₅	nC ₅	C ₆ +	CH ₄ /ΣC ₂₊
Federal1-355A	39.0826	−109.3714	1469	574	Cisco Springs	NAG	Dakota	0.2	nd	0.03	0.1	1.0	3	nd	87.8	4.2	nd	1.6	0.0001	0.7	0.5	0.4	0.2	0.5	14
Federal14-02	39.0623	−109.3443	1435	611	Cisco Springs	NAG	Dakota	0.1	nd	0.02	0.2	2.7	2	nd	88.9	4.3	nd	0.8	nd	0.4	0.1	0.1	0.02	0.3	17
Federal14-7	39.0685	−109.5616	1604	880	Cisco Dome	NAG	Dakota/Morrison	0.1	nd	0.01	0.03	3.5	2	nd	87.3	4.2	0.0003	1.3	0.0004	0.5	0.4	0.3	0.2	0.5	15
Federal13-2	39.0683	−109.5482	1602	785	Cisco Dome	NAG	Dakota/Morrison	0.1	0.5	0.01	0.04	1.9	1	nd	90.7	3.6	0.0002	0.8	0.0002	0.4	0.2	0.2	0.1	0.3	20
Federal24-2	39.0576	−109.5531	1593	884	Cisco Dome	NAG	Dakota/Morrison	0.2	nd	0.01	0.04	0.6	2	nd	94.0	2.6	0.0001	0.5	0.0002	0.2	0.1	0.1	0.04	0.1	29
TXO14-1	39.0616	−109.3485	1428	687	Cisco Springs	OAG	Dakota/Entrada	0.03	nd	0.01	0.2	4.3	1	nd	88.9	3.5	nd	0.6	0.0004	0.5	0.3	0.4	0.1	0.6	21
Federal31-1A	39.0286	−109.5296	1518	719	Cisco Dome	NAG	Dakota/Morrison	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Union Gorit II-1	39.0503	−109.5532	1557	778	Cisco Dome	NAG	Morrison	0.1	nd	0.01	0.02	0.5	2	nd	93.8	2.7	0.0001	0.5	0.0002	0.2	0.1	0.1	0.03	0.2	29
AM-11	–	–	1993	1279	Andy's Mesa	NAG	Cutler	0.1	0.04	0.1	1.4	0.03	7	nd	88.3	2.1	0.001	0.5	0.0001	0.1	0.1	0.1	0.04	0.05	33
AM-38	38.0543	−108.6429	1950	1660	Andy's Mesa	NAG	Cutler	0.1	nd	0.2	4.4	0.1	19	nd	74.3	0.9	0.001	0.2	nd	0.1	0.1	0.04	0.03	0.1	61
AM-61	38.0245	−108.6112	2009	1705	Andy's Mesa	NAG	Cutler	0.2	nd	0.03	0.1	0.01	13	nd	83.7	2.0	0.001	0.2	nd	0.1	0.1	0.03	0.02	0.1	36
AM-62a	38.0245	−108.6112	1993	1711	Andy's Mesa	NAG	Cutler	0.2	0.1	0.1	0.9	0.03	17	nd	79.9	1.7	0.0003	0.1	nd	0.03	0.03	0.01	0.01	0.01	43
AM-62b	38.0245	−108.6112	2009	1711	Andy's Mesa	NAG	Cutler	0.2	0.02	0.03	0.1	0.01	14	nd	83.1	1.9	0.001	0.2	nd	0.03	0.1	0.02	0.02	0.05	38
HC-1-36	38.1109	−108.4749	2067	1255	Hamilton Creek	NAG	Cutler	0.4	0.04	0.04	0.05	0.02	18	nd	75.6	1.7	0.001	0.8	0.0004	0.6	0.8	0.6	0.5	0.7	23
AM-75a	38.0391	−108.6334	1958	2104	Andy's Mesa	NAG	Honaker Trail	0.1	0.04	0.03	0.6	0.03	6	nd	89.8	2.2	0.0002	0.5	nd	0.1	0.2	0.1	0.1	0.1	32
AM-75b	38.0391	−108.6334	1973.5	2208	Andy's Mesa	NAG	Honaker Trail	0.1	nd	0.01	0.1	0.1	5	nd	91.5	2.2	0.0003	0.5	nd	0.1	0.2	0.1	0.1	0.2	32
FF-4-20	–	–	–	–	Andy's Mesa	–	Honaker Trail	nd	nd	nd	0.1	0.03	6	nd	92.5	1.1	nd	0.3	na	0.1	0.1	0.1	0.05	0.2	65
FF-4-20	–	–	–	–	Andy's Mesa	–	Honaker Trail	nd	nd	nd	0.1	0.03	6	nd	92.3	1.1	nd	0.3	na	0.1	0.1	0.1	0.04	0.2	63
HC12-13	38.0946	−108.4685	2159	2280	Hamilton Creek	NAG	Honaker Trail	0.0	0.9	0.1	0.5	0.02	8	nd	87.3	1.3	0.0002	0.6	nd	0.3	0.4	0.3	0.1	0.3	38
HC-30-11	38.1296	−108.4611	–	2734	Hamilton Creek	NAG	Honaker Trail	0.1	0.01	0.01	0.04	0.7	4	nd	95.0	0.4	nd	0.04	nd	0.01	0.01	0.01	0.005	0.02	200
HC-25-22	38.1259	−108.4689	2008	1071	Hamilton Creek	NAG	Honaker Trail	0.1	0.01	0.01	0.1	0.6	4	nd	94.9	0.5	nd	0.1	nd	0.02	0.01	0.01	0.01	0.02	174
HC-36-23	38.1100	−108.4705	2084	2399	Hamilton Creek	NAG	Honaker Trail	0.05	nd	0.01	0.05	0.3	3	nd	95.3	1.0	nd	0.3	nd	0.1	0.1	0.1	0.0	0.1	71
HC-36-34	38.1079	−108.4661	2070	2326	Hamilton Creek	NAG	Honaker Trail	0.04	0.01	nd	0.04	0.4	2	nd	96.6	0.7	nd	0.1	nd	0.1	0.05	0.03	0.02	0.04	116
MM31-42	38.2319	−109.2099	2062	1617	Lisbon Valley	OAG	Honaker Trail	0.1	0.01	0.01	0.1	0.02	13	nd	69.2	9.5	0.001	4.1	0.0008	0.6	1.4	0.4	0.6	0.7	5
MM26-34	38.2503	−109.2391	2066	1617	Lisbon Valley	OAG	Honaker Trail	0.1	0.01	0.01	0.05	0.03	10	nd	69.9	12	0.002	4.8	0.002	0.7	1.5	0.4	0.5	0.4	4
MM36-14	38.2428	−109.2207	–	2082	Lisbon Valley	OAG	Honaker Trail	0.14	na	na	na	0.1	8	na	75.0	10	na	4.0	na	0.5	1.1	0.3	0.3	0.6	5
BI24-31	38.1690	−109.1340	1920	947	Lisbon Valley	OAG	Honaker Trail	0.1	0.01	0.02	0.1	0.1	6	nd	93.2	0.01	nd	0.0	nd	0.003	0.01	0.002	0.003	0.02	3204
BH10-31	38.1922	−109.1719	2071	1184	Lisbon Valley	OAG	Honaker Trail	0.0	nd	0.03	0.8	0.3	6	nd	75.6	10	0.001	4.0	0.0017	0.7	1.1	0.2	0.2	0.2	5
Sahgzie 1	37.1696	−109.3064	1446	1954	Greater Aneth	OAG	Paradox (Desert Creek)	0.0	0.01	0.02	0.5	0.1	2	nd	51.3	16	nd	14	nd	2.6	6.8	2.3	2.3	2.1	1
Monument-8n-2	37.3163	−109.1979	1664	1895	Greater Aneth	OAG	Paradox (Desert Creek)	0.0	nd	0.05	1.3	0.1	3	nd	64.9	15	nd	8.5	nd	1.1	3.1	0.8	0.9	0.9	2
McIntyre 17-21	38.0772	−108.9913	1903	2586	Lisbon Valley	OAG	Leadville	0.8	0.1	0.1	0.7	7.1	13	nd	72.5	3.1	nd	1.4	nd	0.5	0.5	0.3	0.1	0.2	15
Lisbon B-610	38.1982	−109.2771	2022	2368	Lisbon Valley	OAG	Leadville	0.1	nd	0.02	0.04	2.0	4	nd	80.3	12	0.001	0.8	nd	0.1	0.15	0.04	0.05	0.1	6
Lisbon D8-10	38.1902	−109.2687	2014	2441	Lisbon Valley	OAG	Leadville/McCracken	0.5	0.5	0.05	0.05	49	11	nd	29.0	6.7	nd	2.1	nd	0.3	0.7	0.2	0.2	0.2	3
Lisbon B8-10	38.1901	−109.2759	1950	2610	Lisbon Valley	OAG	McCracken	0.5	0.03	0.05	0.02	1.2	16	nd	59.0	12	nd	6.4	0.0002	1.0	2.1	0.5	0.5	0.3	3
Lisbon 10-33a	38.1915	−109.2737	1972	2702	Lisbon Valley	OAG	McCracken	0.2	nd	0.1	1.4	3.0	12	nd	60.5	12	nd	6.4	nd	1.0	1.9	0.5	0.4	0.2	3
Lisbon 10-33b	38.1915	−109.2736	1972	2702	Lisbon Valley	OAG	McCracken	0.3	nd	0.04	0.04	4.4	10	nd	59.7	14	nd	7.5	nd	1.13	2.43	0.6	0.6	0.3	3

Abbreviations: NAG - Non-Associated Gas; OAG - Oil-associated Gas; nd - non-detected; na - not-analyzed.

Table 2

Gas compound specific isotopic compositions of natural gases in the Paradox Basin.

Sample/well ID	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	$\delta\text{D}_{\text{H}_2\text{O}}$ (‰)	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	$\delta\text{D}_{\text{CH}_4}$ (‰)	$\delta^{13}\text{C}_{\text{C}_2}$ (‰)	$\delta\text{D}_{\text{C}_2}$ (‰)	$\delta^{13}\text{C}_{\text{C}_3}$ (‰)	$\delta\text{D}_{\text{C}_3}$ (‰)	$\delta^{13}\text{C}_{\text{nC}_4}$ (‰)	$\Delta^{13}\text{CH}_3\text{D}$ (‰)	$2\sigma^2$ (‰)	$T_{13\text{D}}$ (°C)	+	–
Dakota/Morrison [Cisco field]														
Federal11-355A	20.4	na	–44.0	–240.6	–27.2	–151.7	–22.1	–124.2	–23.4	3.5	0.3	129	17	15
Federal14-02	22.5	–66.2	–46.0	–229.5	–25.5	–150.9	–20.2	–107.0	–22.2*	3.5	0.3	127	16	15
Federal14-7	19.0	–61.5	–42.2	–230.2	–26.7	–152.1	–24.2	–130.0	–25.9	3.0	0.3	162	25	23
Federal13-2	14.7	na	–42.3	–223.9	–26.4	–154.5	–21.2	–113.3	–24.1	3.6	0.5	121	34	28
Federal24-2	15.7	na	–41.9	–224.8	–26.5	–151.8	–23.0	–125.5	–25.3	3.3	0.3	140	18	16
TXO14-1	14.1	–61.8	–50.6	–242.8	–23.6	–134.8	–18.8*	–103.0	–22.9	4.5	0.2	76	8	8
Federal31-1A	nd	na	–44.8	–247.5	na	na	na	na	na	3.2	0.1	146	9	8
Union Gorit II-1	15.7	na	–42.5	–230.7	–26.5	–153.3	–22.8	–121.4	–24.9	3.0	0.3	161	20	18
Cutler [Andy's Mesa and Hamilton Creek fields]														
AM-11	nd	na	–33.7	–135.0	–28.3	–116.7	–25.4	–111.7	–25.8	na	na	na	na	na
AM-38	nd	–25.9	–30.0	–125.6	–30.6	–124.3	–26.3*	–93.0*	–23.8*	2.6	0.2	195	18	20
AM-61	nd	–125.9 ^a	–32.6	–134.1	–24.3	–87.2	–20.4*	–33.0*	–20.5*	2.6	0.3	193	22	25
AM-62a	nd	na	–	–	–23.9	–78.9	–19.9	nd	nd	–	–	–	–	–
AM-62b	nd	–125.9	–32.7	–135.1	–24.3	–83.1	–21.7*	–29.0*	–23.9*	2.7	0.2	183	17	18
HC-1-36	nd	–60.3	–32.3	–130.1	–25.9	–111.9	–23.9	–111.2	–23.7	2.6	0.1	191	11	10
Honaker Trail [Andy's Mesa and Hamilton Creek fields]														
AM-75a	nd	na	na	na	–28.5	–117.5	–24.7	nd	–24.5	na	na	na	na	na
AM-75b	nd	–33.0	–34.3	–135.3	–28.7	–118.7	–24.7	–111.3	–24.1*	2.7	0.1	190	13	14
FF-4-20	na	na	–32.6	–130.2	–30.7	na	–25.0	na	na	na	na	na	na	na
FF-4-20	na	na	–32.5	–130.2	–30.5	na	–25.3	na	na	na	na	na	na	na
HC12-13	nd	–48.7	–34.4	–129.6	na	na	na	na	na	5.2	0.3	47	13	13
HC-30-11	–7.0	na	–32.0	–128.2	–33.0	–122.8	–25.0*	nd	–20.3*	2.7	0.2	182	19	18
HC-25-22	–7.4	–52.6	–32.6	–128.2	–32.3	–140.0	–23.9*	nd	–20.4*	3.0	0.1	160	9	9
HC-36-23	–7.1	na	–34.2	–128.8	–29.1	–130.0	–24.6	nd	–23.1*	3.0	0.3	163	24	22
HC-36-34	–6.8	–41.0	–34.7	–128.5	–30.0	–135.0	–24.9	nd	–23.2*	3.0	0.3	163	20	18
Honaker Trail [Lisbon Valley field]														
MM31-42	nd	–47.0	–25.6	–108.2	–32.0	–138.3	–28.5	–106.8	–27.7	2.5	0.7	200	79	56
MM26-34	nd	–38.2	–43.0	–194.9	–31.7	–134.6	–28.7	–106.9	–27.7	1.7	0.3	297	50	41
MM36-14	na	na	–29.6	–27.9	na	na	na	na	na	na	na	na	na	na
BI24-31	nd	–48.1	–45.2	–231.9	nd	nd	nd	nd	nd	2.9	0.2	165	13	12
BH10-31	nd	–74.9	–42.6	–197.2	–30.2	–127.5	–27.2	–105.5	–26.5	na	na	na	na	na
Paradox [Greater Aneth field]														
Sahgzie 1	nd	–32.9	–45.5	–284.1	–36.4	–199.7	–32.6	–143.1	–30.4	0.9	0.4	485	155	100
Monument-8n-2	nd	–34.6	–44.9	–259.7	–36.2	–186.8	–32.7	–140.1	–30.7	0.3	0.5	825	na	323
Leadville/McCracken [Lisbon Valley field]														
McIntyre 17-21	–7.0	–80.6	–37.1	–130.1	–28.5	–118.0	–25.6	–111.7	–24.0	2.1	0.3	247	43	36
Lisbon B-610	–7.4	–67.3	–37.7	–155.7	–32.5	–130.9	–29.2	–108.1	–27.9	2.0	0.3	264	40	34
Lisbon D8-10	–6.9	–59.6	–41.4	–154.6	–34.1	–106.3	–29.4	–101.6	–27.2	2.0	0.2	261	34	30
Lisbon B8-10	–8.4	–63.2	–47.5	–216.7	–36.1	–135.3	–32.2	–114.3	–30.0	1.3	0.3	374	65	49
Lisbon 10-33a	–7.8	–35.1	–45.7	–192.3	–35.0	–121.7	–31.1	–104.2	–28.9	na	na	na	na	na
Lisbon 10-33b	–9.0	–29.2	–45.8	–191.8	–35.4	–124.1	–31.4	–110.1	–29.2	2.0	0.2	256	28	25

 $2\sigma^2$ of $\Delta^{13}\text{CH}_3\text{D}$ based on 95% CI. $T_{13\text{D}}$ – Apparent temperatures.

nd – non-detected due to low molecular compositions.

na – not-analyzed.

^a $\delta\text{D}_{\text{H}_2\text{O}}$ data from the “AM-62b” sample in the same Andy's Mesa field with corresponding geological formation.

* Carbon and/or hydrogen isotope data obtained online via GC-C-IRMS and/or GC-P-IRMS.

(Wang et al., 2015). Samples were then analyzed relative to a reference gas (commercially sourced methane ‘AL1’) for 7 to 12 acquisition cycles (sample-standard pairs). The $\delta^{13}\text{C}$ and δD values of the reference gas (AL1) are reported in V-PDB and V-SMOW scale, calibrated against community reference NGS-1 and NGS-3, and the value of $\Delta^{13}\text{CH}_3\text{D}$ is calibrated by equilibrating a set of reference gas at 250 °C (Wang et al., 2015).

The values of $\delta^{13}\text{C}$ and δD of methane were derived from the

measurements of isotopologue abundances. The ratio of isotopologues and the ratio of isotopes are transposable such that $^{12}\text{C}/^{13}\text{C}$ is equivalent to $[^{13}\text{CH}_3\text{D}/^{12}\text{CH}_4]$, and D/H is equivalent to $1/4[^{12}\text{CH}_3\text{D}/^{12}\text{CH}_4]$.

$\Delta^{13}\text{CH}_3\text{D}$ represents the deviation of the abundance of clumped isotopologue $^{13}\text{CH}_3\text{D}$ from the stochastic distribution, such that

$$\Delta^{13}\text{CH}_3\text{D} = \ln \frac{[^{13}\text{CH}_3\text{D}][^{12}\text{CH}_4]}{[^{13}\text{CH}_4][^{12}\text{CH}_3\text{D}]} \quad (1)$$

and is reported in per mil (‰) units.

$\Delta^{13}\text{CH}_3\text{D}$ at isotopic equilibrium as a function of temperature was computed via the following equation (valid above 270 K) from Eldridge et al. (2019):

$$\Delta^{13}\text{CH}_3\text{D}(T) \cong 1000 \times \ln(K^{13}\text{CH}_3\text{D}) = \frac{1.47348 \times 10^{19}}{T^7} - \frac{2.08648 \times 10^{17}}{T^6} + \frac{1.19810 \times 10^{15}}{T^5} - \frac{3.54757 \times 10^{12}}{T^4} + \frac{5.54476 \times 10^9}{T^3} - \frac{3.49294 \times 10^6}{T^2} + \frac{8.89370 \times 10^2}{T} \quad (2)$$

These $\Delta^{13}\text{CH}_3\text{D}$ -based temperatures (T) are herein called ‘apparent temperatures (T_{13D})’.

δD values of formation water ($\delta\text{D}_{\text{H}_2\text{O}}$; Table 2) from corresponding wells were previously reported in Kim et al. (2022a). $\delta\text{D}_{\text{H}_2\text{O}}$ values were measured at the University of Arizona via laser spectrometer (Los Gatos Research DLT-100 Liquid Water Isotope Analyzer) with a precision of 0.5‰ or isotope ratio mass spectrometer (Finnigan Delta S) with a precision of 1.0‰.

Forward models for $\Delta^{13}\text{CH}_3\text{D}$ were constructed based on the burial/thermal histories of the basin (Fig. 2) to calculate the temporal evolution of methane isotopologue compositions using equilibrium fractionation factors and the rate of hydrogen (D/H) isotope exchange between CH_4 and H_2O . Model inputs are initial isotope and isotopologue compositions of methane ($\delta^{13}\text{C}$, δD , and $\Delta^{13}\text{CH}_3\text{D}$) and the thermal histories of source rocks in different locations and depths of the basin. Hydrogen equilibrium fractionation factors for CH_4 in gas phase and H_2O as a function of temperature (T in Kelvin) were calculated using the following equations valid from 3 to 200 °C from Turner et al. (2021):

$$1000 \times \ln^D a_{\text{CH}_4(\text{g})-\text{H}_2\text{O}(\text{l})} = -\frac{7.9443 \times 10^{12}}{T^4} + \frac{8.7772 \times 10^{10}}{T^3} - \frac{3.4973 \times 10^8}{T^2} + \frac{5.4398 \times 10^5}{T} - 382.05 \quad (3)$$

Isotopic exchange rate followed abiotic exchange rate constants (units of $\ln(\text{sec}^{-1} [\text{mol/L}]^{-1})$ versus $1000/T$ (K^{-1})) from Turner et al. (2022):

$$\ln(k_r) = -17.32 \times (1000/T) + 3.19 \quad (4)$$

The approach is similar to Beaudry et al. (2021) who calculated the equilibration timescales at constant temperatures. Here, we used the source rocks’ thermal history from basin models, which were based on Rock-Eval pyrolysis and vitrinite reflectance (Nuccio and Condon, 1996) and apatite (U-Th)/He age data (Hoffman, 2009), and applied updated isotopic exchange rates and fractionation factors (Turner et al., 2021; Turner et al., 2022). The forward model was applied for three different parts of the basins: 1) Cane Creek source rocks of the Paradox Formation in the Lisbon Valley field, northeastern side of the basin (Nuccio and Condon, 1996); 2) Ismay-Desert Creek source rocks of the Paradox Formation in the Greater Aneth field, southwestern side of the basin (Nuccio and Condon, 1996); and 3) Cretaceous sediments in the Cisco field (based on thermochronology constraints from the Hay Canyon area, Book Cliffs; Hoffman, 2009).

4. Results

4.1. Traditional molecular and isotope ratios of natural gas

Measured molecular and isotopic composition of natural gas samples from six different reservoirs across the Paradox Basin are reported in Tables 1 and 2. Gas samples were collected from within the Ismay-Desert Creek source rocks of Paradox Formation in the southwestern part of the basin (e.g., Greater Aneth field), while gas samples were collected from

several reservoirs above/below the Cane Creek source rocks of the Paradox Formation in the northeastern part of the basin (Lisbon, Andy’s Mesa, and Hamilton Creek fields) and Cisco field. Methane (CH_4) is the dominant component in most gas samples (51.3–96.6 mol%), except for the Lisbon D8-10 sample with 29.0 mol% CH_4 and a remarkable 49 mol% CO_2 (Table 1). Gases have variable amounts of C_2 (0.01–16.2 mol%), C_3 (0.01–13.7 mol%), and nC_4 (0.01–6.8 mol%) (Table 1). The methane to higher chain hydrocarbons ratios ($\text{CH}_4/\Sigma\text{C}_{2+}$ or dryness) range from 1.4 to 61, except for the BI24-31 sample with 3204 (Table 1 and Fig. 3).

$\delta^{13}\text{C}_{\text{CH}_4}$ values for all samples range from –50.6 to –25.6‰ (Table 2 and Fig. 3). The $\delta^{13}\text{C}_{\text{C}_2}$ values for all samples range from –36.4 to –23.6‰, while the $\delta^{13}\text{C}_{\text{C}_3}$ values range from –32.7 to –18.8‰ and are more positive than their respective $\delta^{13}\text{C}_{\text{C}_2}$ values (Table 2 and Fig. 4). The $\delta^{13}\text{C}_{\text{nC}_4}$ values range from –30.7 to –20.3‰. The variation of $\delta^{13}\text{C}$ values of CH_4 through C_4 for each gas sample was compared to expected trends for natural gas derived from a single source without post-genetic alteration and/or mixing effects (dashed straight lines in Fig. 4; Rooney et al., 1995; Chung et al., 1988; and Burruss and Laughrey, 2010). The gases from the shallower Dakota, Morrison, Cutler, and Honaker Trail formations have lower C_2 and C_3 concentrations and higher $\delta^{13}\text{C}_{\text{C}_2}$ and $\delta^{13}\text{C}_{\text{C}_3}$ values than those from deeper Paradox, Leadville, and McCracken formations (Fig. 5A–5C). The isotopic difference between $\delta^{13}\text{C}_{\text{C}_2}$ and $\delta^{13}\text{C}_{\text{C}_3}$ ($\Delta^{13}\text{C}_{\text{C}_2/\text{C}_3}$) of most samples is similar, while C_2/C_3 molar ratios vary from 1 to 16 (Fig. 5D). $\delta\text{D}_{\text{CH}_4}$ values for all samples range from –284.1 to –108.2‰ (Fig. 6A).

Relatively high CO_2 (0.5–4.3 mol%, Table 1) concentrations from the Dakota and Morrison formations exhibit very high $\delta^{13}\text{C}_{\text{CO}_2}$ values of 14.1 to 22.5‰ (Table 2 and Fig. 6B). Gases from the Leadville and McCracken formations contain the highest He (0.2–0.8 mol%), Ar (0.02–0.09 mol%), N_2 (11–16 mol%), and CO_2 (1.2–49 mol%, a median 3.7 mol%) concentrations in this study (Table 1) with $\delta^{13}\text{C}_{\text{CO}_2}$ values of –8.3 to –6.9‰ (Table 2 and Fig. 6B). CO_2 concentrations from the Honaker Trail Formation in the Hamilton Creek field are higher (up to 0.7 mol%) than the same formation in Lisbon Valley and Andy’s Mesa fields (<0.3 mol%). Their $\delta^{13}\text{C}_{\text{CO}_2}$ values (–7.4 to –6.8‰) are nearly identical to those from the Leadville and McCracken formations. Gases from the Cutler Group also exhibit high He (0.1–0.4 mol%), Ar (0.03–0.19 mol%), and N_2 (7–19 mol%), but low CO_2 (0.01–0.09 mol%) concentrations (Table 1). CO_2 concentrations from some formation gases (Cutler Group and Honaker Trail Formation in the Lisbon Valley field and the Paradox Formation in the Greater Aneth field) were too low for $\delta^{13}\text{C}_{\text{CO}_2}$ analysis.

4.2. Clumped isotopologues of methane

The abundance of $\Delta^{13}\text{CH}_3\text{D}$ can help constrain the temperature at which methane was formed and/or last equilibrated (Ono et al., 2014; Wang et al., 2015; Xie et al., 2021). Methane clumped isotopologue ($\Delta^{13}\text{CH}_3\text{D}$) values for the Dakota and Morrison formations range from 3.0 to 4.5‰, corresponding to apparent temperatures (T_{13D}) between 76 and 162 °C (Table 2 and Fig. 7A). The $\Delta^{13}\text{CH}_3\text{D}$ values for gases from the Cutler Group and/or Honaker Trail Formation are consistent (2.4 to 2.9‰), corresponding to T_{13D} from 161 to 202 °C, except for the HC12-13 ($\Delta^{13}\text{CH}_3\text{D} = 5.2$ ‰; $T_{13D} = 47$ °C) and MM26-34 ($\Delta^{13}\text{CH}_3\text{D} = 1.7$ ‰; $T_{13D} = 297$ °C) samples. Gases from the Paradox Formation have very low $\Delta^{13}\text{CH}_3\text{D}$ values (0.9 and 0.3‰) corresponding to environmentally unrealistic T_{13D} (485 and 825 °C, respectively). Gases from the Leadville and/or McCracken formations also show low consistent $\Delta^{13}\text{CH}_3\text{D}$ values (2.0–2.1‰), corresponding to T_{13D} from 247 to 264 °C, except for the Lisbon B8-10 sample with a lower $\Delta^{13}\text{CH}_3\text{D}$ (1.3‰; $T_{13D} = 374$ °C).

$\Delta^{13}\text{CH}_3\text{D}$ values were plotted versus the isotopic enrichment factor (ϵ) between δD values of methane and formation water ($\epsilon_{\text{methane/water}}$) (Fig. 7B). The isotopic equilibrium curve, shown in Fig. 7B was calculated using the $\Delta^{13}\text{CH}_3\text{D}$ (Eq. (2)) and $\epsilon_{\text{methane/water}}$ (Eq. (3)) calibrations given by Eldridge et al. (2019) and Turner et al. (2021), respectively. Gases from the Paradox Formation in the Greater Aneth field plot below

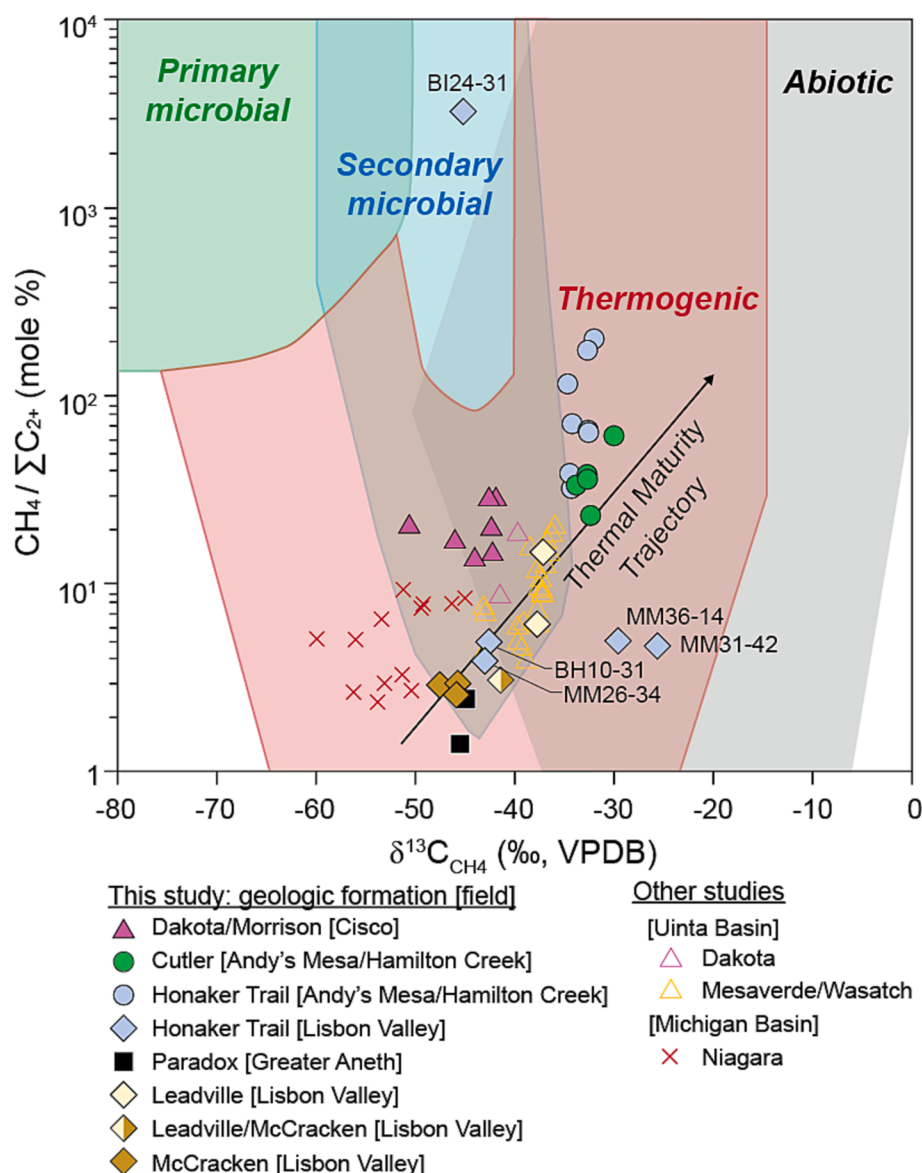


Fig. 3. $\delta^{13}\text{C}_{\text{CH}_4}$ versus $\text{CH}_4/\Sigma\text{C}_{2+}$ of the ‘Bernard plot’ with distinct sections of microbial, thermogenic, and abiotic gases as well as a thermal maturation trend (Bernard et al., 1976; Giunta et al., 2019; Milkov and Etiope, 2018; McIntosh et al., 2018). Thermogenic gas data from the Dakota and Mesaverde/Wasatch formations of the Uinta Basin (Zhang et al., 2009) and Silurian Niagara Formation of the Michigan Basin (Martini et al., 1998; Giunta et al., 2019).

the isotopic equilibrium curve, while gases from the Dakota and Morrison formations in the Cisco field and the Honaker Trail and McCracken formations in the Lisbon Valley field plot close to the equilibrium curve. Gases from the Cutler Group and Honaker Trail Formation in the Andy’s Mesa and Hamilton Creek fields and Leadville Limestone in the Lisbon Valley field plot above the equilibrium curve. One of the Honaker Trail Formation samples (HC12-13) from the Hamilton Creek field plots far from the equilibrium curve with an anomalously high $\Delta^{13}\text{CH}_3\text{D}$ (5.2‰) value.

The evolution of $\Delta^{13}\text{CH}_3\text{D}$ values through geologic time was modeled for three fields (Lisbon Valley, Greater Aneth, and Cisco fields) using their thermal histories of source rocks from basin models and a rate of abiotic hydrogen (D/H) isotope equilibration between methane and water (Turner et al., 2022) (Fig. 8). In the models for the Lisbon Valley field, methane in the Cane Creek source rocks of the Paradox Formation was equilibrated during maximum burial (~30–80 Ma) at 160 to 170 °C (Fig. 8A). Hydrogen isotopes of methane and water within the source rocks in the Lisbon Valley field were isotopically equilibrated for ~30 m.y. during maximum burial (~30–60 Ma). In the models for

the Greater Aneth field, the $\Delta^{13}\text{CH}_3\text{D}$ and $\varepsilon_{\text{methane/water}}$ values of methane, in the Ismay-Desert Creek source rocks of the Paradox Formation, slightly increased during burial (25–80 Ma; up to 110 °C), but never reached equilibrium, and then maintained their values after cooling (Fig. 8B). In the models for the Cisco field, three thermal histories for the Cretaceous sediments were applied to the models, starting around 100 Ma, during maximum burial with different initial maximum temperatures ($T_0 = 110, 140, \text{ or } 160^\circ\text{C}$) (Fig. 8C). While the model starting at 110 °C T_0 never achieved $\Delta^{13}\text{CH}_3\text{D}$ equilibrium, the models starting at 140 and 160 °C reached $\Delta^{13}\text{CH}_3\text{D}$ equilibrium during maximum burial until 50–60 Ma. The model results starting at 160 °C T_0 show hydrogen isotopic equilibrium between methane and water during the (first) maximum burial (~60–70 Ma), while those starting at 140 °C T_0 exhibit hydrogen isotopic equilibrium during the secondary burial maximum (~10–50 Ma). The three modeled $\Delta^{13}\text{CH}_3\text{D}$ results at present (3.1–3.4‰) are within the range of the measured $\Delta^{13}\text{CH}_3\text{D}$ values (2.9–4.4‰).

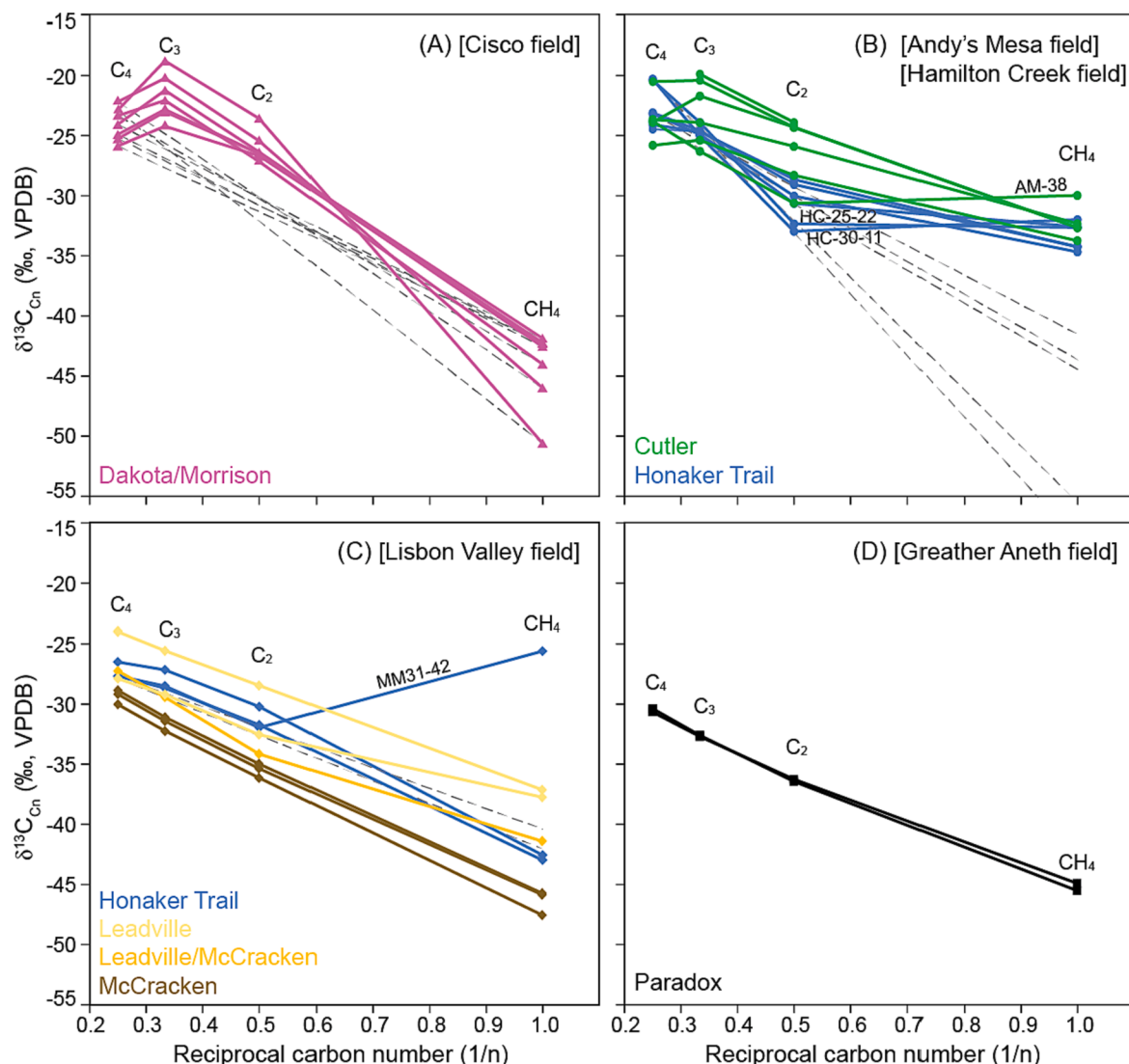


Fig. 4. $\delta^{13}\text{C}_n$ ($n = 1$ to 4) as a function of the reciprocal carbon number ($1/n$) of hydrocarbons of each sample. A-D diagrams display specific fields with various reservoirs shown in different colored lines. The dashed straight line for select gas samples represents the expected $\delta^{13}\text{C}$ trend for natural gases derived from a single source without post-genetic alteration and/or mixing effects (e.g., Chung et al., 1988; Rooney et al., 1995; Burruss and Laughrey, 2010).

5. Discussion

5.1. Thermogenic origin of most natural gas

Natural gases in oil and gas reservoirs across the Paradox Basin plot within the thermogenic gas field in the ‘Bernard plot’ (Fig. 3; Bernard et al., 1976; Milkov and Etiope, 2018) with low $\text{CH}_4/\Sigma\text{C}_{2+}$ and high $\delta^{13}\text{C}_{\text{CH}_4}$ values, indicating natural gases are predominantly thermogenic in origin. Many of the thermogenic gases appear to have originated from a single source rock, as their $\delta^{13}\text{C}_n$ values follow a straight trend in Fig. 4 (e.g., Honaker Trail and Leadville/McCracken formations in the Lisbon Valley field and Paradox Formation in the Greather Aneth field). Both $\Delta^{13}\text{C}_{\text{C}_2/\text{C}_3}$ and C_2/C_3 molar ratios of most natural gases are within the range of modeled values for the secondary cracking of oil from Type II kerogen at 200 °C (Prinzhofer and Huc, 1995; Lorant et al., 1998) (Fig. 5D). Many of the $\Delta^{13}\text{CH}_3\text{D}$ (and apparent methane formation temperatures, $T_{13\text{D}}$) and $\delta^{13}\text{C}_{\text{CH}_4}$ values are also within the prior range of thermogenic gases from other basins (Wang et al., 2015; Douglas et al., 2016, 2017; Giunta et al., 2019; McIntosh et al., 2018) (Fig. 7A).

The predominance of thermogenic gas is consistent with the deep burial history of black shale source rocks, interbedded in evaporite

confining units in the Paradox Formation, throughout most of the basin. The sterilization of shale source rocks and adjacent conventional reservoirs during maximum burial (>80 °C; Head et al., 2003; Wilhelms et al., 2001) and lack of meteoric water influx (Kim et al., 2022a, 2022b) likely precluded widespread microbial gas generation in the organic-rich shales (McIntosh et al., 2023).

5.2. Different thermal maturities of hydrocarbons

Most natural gases in the Paradox Basin follow a typical thermal maturation trend in gas molecular and isotopic composition (Giunta et al., 2019; Milkov and Etiope, 2018; McIntosh et al., 2018) with increasing thermal maturity (Figs. 3 and 5C). The thermogenic gas trend in the $\delta^{13}\text{C}_{\text{C}_2}$ versus $\delta^{13}\text{C}_{\text{C}_3}$ plot (Fig. 5C) (Martini et al., 2003; Osborn and McIntosh, 2010) shows similar differences in thermal maturity from the $\text{CH}_4/\Sigma\text{C}_{2+}$ versus $\delta^{13}\text{C}_{\text{CH}_4}$ plot (Fig. 3). For example, oil-associated gases from the Paradox Formation in the Greather Aneth field, in the southwestern part of the basin, show the lowest thermal maturity with relatively wet gas (1.4 and 2.4 of $\text{CH}_4/\Sigma\text{C}_{2+}$) and low $\delta^{13}\text{C}_{\text{CH}_4}$ ($-45.2 \pm 0.4\text{‰}$), $\delta^{13}\text{C}_{\text{C}_2}$ ($-36.3 \pm 0.1\text{‰}$), and $\delta^{13}\text{C}_{\text{C}_3}$ ($-32.7 \pm 0.1\text{‰}$) values, compared to other samples in the basin. The anomalously low $\Delta^{13}\text{CH}_3\text{D}$

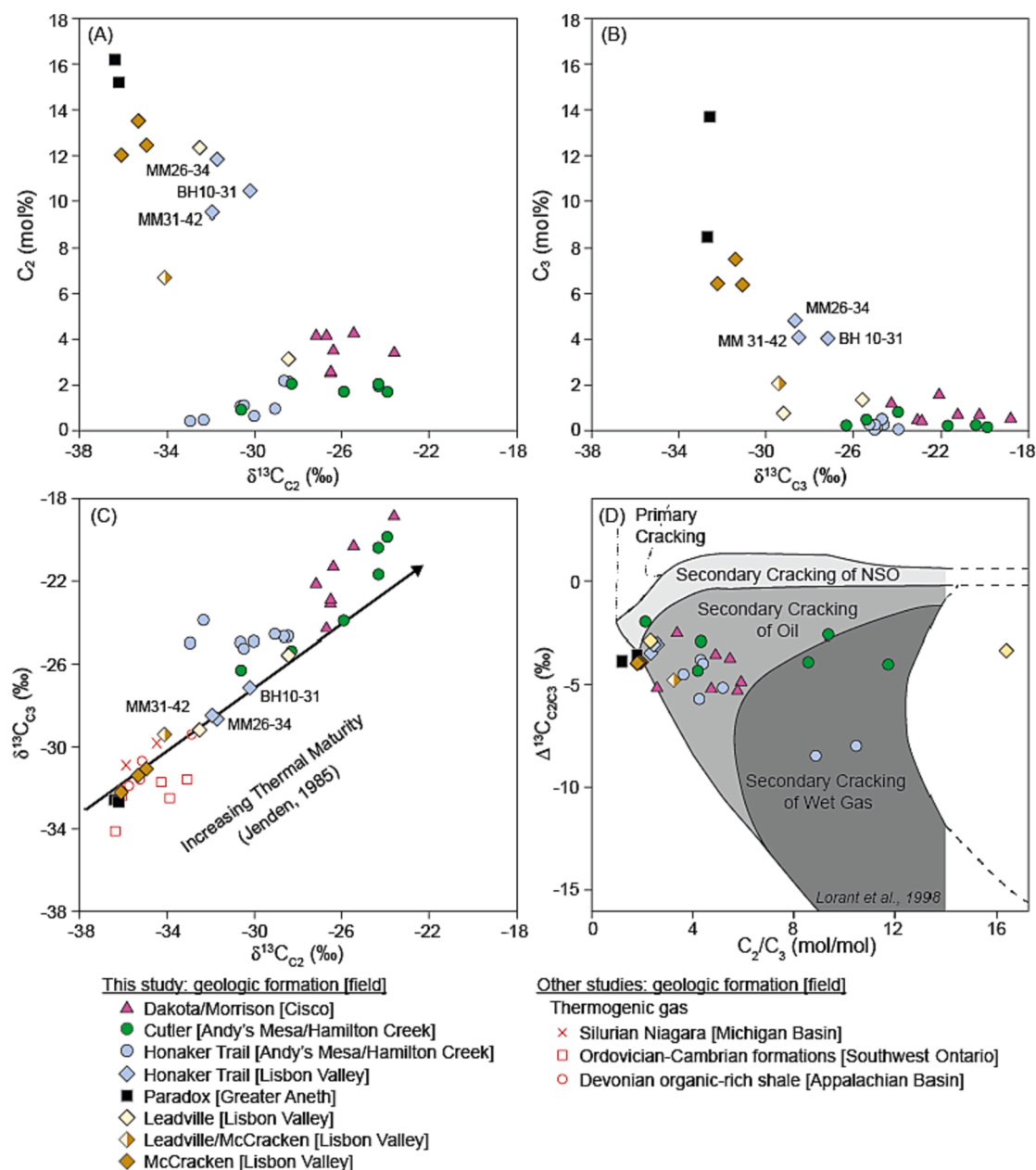


Fig. 5. (A) Ethane (C_2) concentration (mole %) versus $\delta^{13}C$ values of C_2 . (B) Propane (C_3) concentration (mole %) versus $\delta^{13}C$ values of C_3 . (C) C isotopic relationship between C_2 and C_3 . Thermogenic gas data from Ordovician-Cambrian formations in southwestern Ontario and Silurian Niagara Formation in the Michigan Basin (Giunta et al., 2019), and Devonian organic-rich shales in the Appalachian Basin (Osborn and McIntosh, 2010). (D) Evolution of the maturity model at 200 °C with four thermal maturity zones (Lorant et al., 1998).

values (Fig. 7), corresponding to unrealistically high T_{13D} (485 to 825 °C) relative to the thermal history for the Paradox Formation in the Greater Aneth field (Fig. 2B), indicate that the relatively low-maturity thermogenic methane (Figs. 1B, 3, and 5C) never reached thermal equilibrium. This is reasonable considering the relatively shallow burial depths of source rocks (Isamay-Desert Creek member of Paradox Formation) with lower $R_0 \leq 0.87\%$ (Fig. 1B) along the southwestern margin of the basin, compared to the more deeply buried source rocks in the northeastern part of the basin (Fig. 2A). The high T_{13D} values are beyond the thermogenic gas window (300 °C), suggesting that disequilibrated $\Delta^{13}CH_3D$ cannot serve as a thermometer for methane generation, but rather as a proxy of thermal maturity (Xie et al., 2021). In addition, this study extends the minimum range of $\Delta^{13}CH_3D$ values for thermogenic gas beyond previous studies (Giunta et al., 2019; Douglas et al., 2017).

Relatively low to moderate thermal maturity gases were observed in

the Leadville and McCracken formations below source rocks (Cane Creek member of Paradox Formation) in the Lisbon Valley field (northeastern part of the basin), based on the increasing $CH_4/\Sigma C_{2+}$ and $\delta^{13}CH_4$ values with decreasing stratigraphic depth. For instance, the McCracken Sandstone is the deepest (2.5–2.9 and $-45.1 \pm 2.3\%$), followed by the Leadville/McCracken formations (3.1 and -41.4%) and the overlying Leadville Limestone (6.1–14.6 and $-37.4 \pm 0.3\%$). The low to moderate thermal maturity gases may have come from early stages of hydrocarbon generation in the source rocks (Fig. 2A). This likely occurred during the deposition of evaporites and siliciclastic sediments and rapid burial, and the expulsion of hydrocarbons into underlying formations, in the deepest part of the sedimentary basin (Fig. 9B). The lack of higher maturity hydrocarbons in these deep reservoirs, suggests they may have been isolated from the overlying shale source rocks of the Paradox Formation, during the growth of the

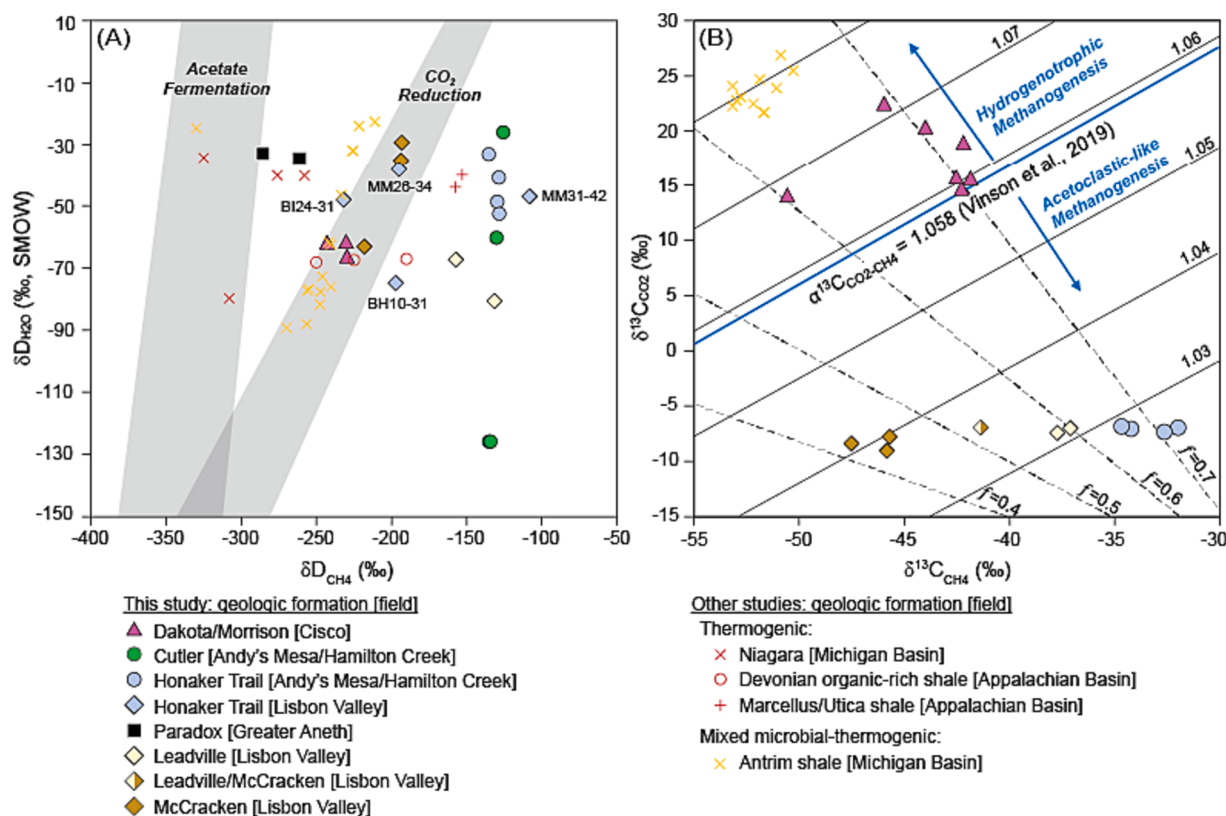


Fig. 6. (A) δD_{CH_4} versus δD_{water} plot with hydrogen isotope fractionation trends of acetate fermentation and CO_2 reduction (modified from Osborn and McIntosh, 2010) forming microbial gases. (B) $\delta^{13}C_{CH_4}$ versus $\delta^{13}C_{CO_2}$ plot with carbon isotope fractionation trends of hydrogenotrophic (i.e., CO_2 reduction) and acetoclastic-like (i.e., acetate fermentation) methanogenesis, distinguished by an alpha fractionation factor ($\alpha^{13}C_{CO_2-CH_4}$) of 1.058 given by Vinson et al. (2019). Examples of thermogenic gases shown as red symbols are from the Silurian Niagara Formation in the Michigan Basin (Giunta et al., 2019), Devonian organic-rich shales in the Appalachian Basin (Osborn and McIntosh, 2010), and Marcellus/Utica shales in the Appalachian Basin (Wang et al., 2015). Examples of mixed microbial-thermogenic gases in yellow symbols are from the Devonian Antrim Shale in the Michigan Basin (Giunta et al., 2019; Stolper et al., 2015). Examples of microbial gases, shown as green symbols, are from the Santa Monica/Santa Barbara basins (Stolper et al., 2015), Northern Cascadia Margin, and Powder River Basin (Wang et al., 2015).

Paradox Formation salt walls. The calculated T_{13D} values (247 to 374 °C; Fig. 7A) are also much higher than expected given the thermal/burial histories of the overlying source rocks ($\sim < 200$ °C in Fig. 2A; Nuccio and Condon, 1996). The early generation, migration, and isolation of these natural gases from the source rocks may have prevented equilibration with $\Delta^{13}CH_3D$. The methane isotopologues are likely recording apparent temperatures that reflect early thermogenic kinetic effects, not equilibrium conditions.

Thermogenic gases from the Honaker Trail Formation above the source rocks in the Lisbon Valley field are slightly more mature (low to moderate extents of thermal maturity) than gases in the Leadville and McCracken formations (Fig. 3). $\delta^{13}C_{CH_4}$ values of the Honaker Trail Formation in the Lisbon Valley field plot along the thermal maturity trend (BH10-33; MM26-34) or below the trend, except for the BI24-31 sample. The $\Delta^{13}CH_3D$ values (2.5 and 2.9‰) correspond to 165 and 200 °C T_{13D} , respectively, except for the MM26-34 sample. These T_{13D} are within the thermogenic gas window (300 °C), indicating the thermally matured gases are equilibrated with $\Delta^{13}CH_3D$ (Fig. 7A).

The Honaker Trail Formation samples (MM31-42; MM36-14) that plot below the thermal maturity trend were likely affected by very wet gas at a low level of maturity when the source rocks behaved as an open system (Burruss and Laughrey, 2010), based on low CH_4/SC_{2+} and high $\delta^{13}C_{CH_4}$ compared to $\delta^{13}C_{C_{2+}}$ values (Figs. 3 and 4C). In Fig. 5C, the MM31-42 sample falls on the thermogenic gas trend together with other Honaker Trail samples (MM26-34; BH10-31) with similar $\delta^{13}C_{C_2}$ and $\delta^{13}C_{C_3}$ values, supporting a similar degree of thermal maturity for gases from the same formation and field.

The BI24-31 sample with very high CH_4/SC_{2+} (Fig. 3) may have been

affected by solubility fractionation through interaction with fluids or migration fractionation during gas leakage or diffusion from source rocks leading to the loss of C_{2+} hydrocarbons (Prinzhofer and Pernaton, 1997; Prinzhofer and Battani, 2003). The relatively high $\Delta^{13}CH_3D$ value of the BI24-31 sample, compared to other Honaker Trail samples in the Lisbon Valley field, also suggests the effects of diffusion (e.g., trajectory in Fig. 7A) (Douglas et al., 2017; Young et al., 2017). Alternatively, anaerobic oxidation of C_{2+} and/or biodegradation of crude oil, producing secondary microbial methane, in this oil-associated gas reservoir could explain the extremely low C_{2+} (0.01 mol%) and high CH_4 (93 mol %) concentrations of the BI24-31 sample (Martini et al., 2003, 2008). It is notable that the $\Delta^{13}CH_3D$, $\delta^{13}C_{CH_4}$, and $\epsilon_{methane/water}$ values of the BI24-31 sample are similar to the Dakota and Morrison formation reservoirs, which are interpreted to contain mixed thermogenic-microbial gases (See Section 5.3 below). The presence of relatively high $\delta^{13}C_{C_{2+}}$ and $\delta^{13}C_{CO_2}$ values could suggest anaerobic oxidation of hydrocarbons, coupled to secondary microbial methanogenesis (Martini et al., 2003; 2008), however the concentrations of C_2 and CO_2 of the BI24-31 sample were too low for $\delta^{13}C$ analysis.

The thermally mature gases in the Honaker Trail Formation in the Lisbon Valley field, in the proximity of isotopic equilibrium in $\Delta^{13}CH_3D$ versus $\epsilon_{methane/water}$ space (Fig. 7B), suggests that post-genetic alteration, resulting in equilibrium with hydrogen isotope exchange, occurred between methane and water or other hydrogen sources (e.g., H_2S). The $\Delta^{13}CH_3D$ values of these thermogenic gases are similar to thermogenic gases in the deep, Silurian Niagara play in the Michigan Basin (Giunta et al., 2019), while the $\epsilon_{methane/water}$ values are different. This implies that the thermal maturity of the gases in the Niagara

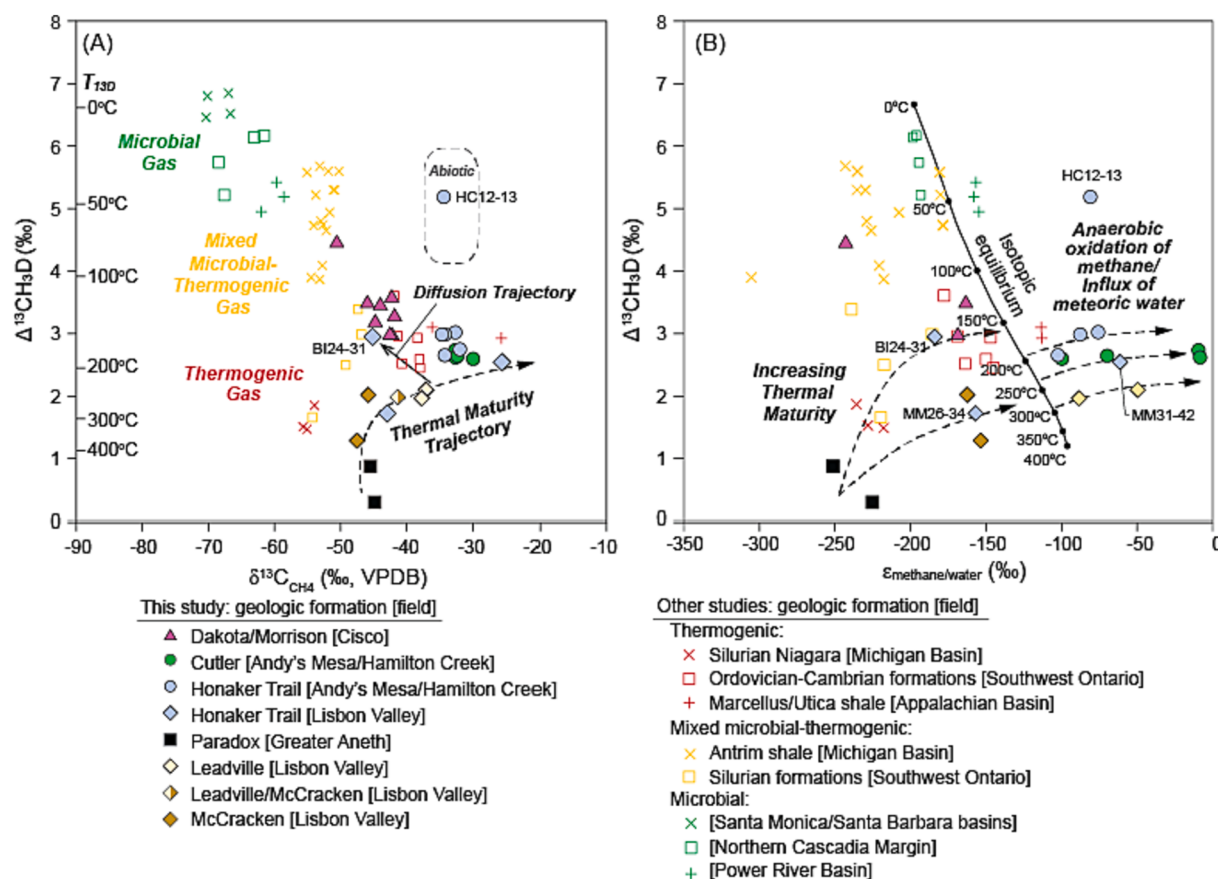


Fig. 7. (A) Methane clumped isotope ($\Delta^{13}\text{CH}_3\text{D}$) values as a function of $\delta^{13}\text{C}$ of methane with compiled fields for microbial, mixed microbial-thermogenic, and thermogenic gases in sedimentary basins (Stolper et al., 2014a, b; Stolper et al., 2015; Wang et al., 2015; Douglas et al., 2016; Young et al., 2017; Giunta et al., 2019; Shuai et al., 2018; McIntosh et al., 2018). Diffusion trajectory given by Douglas et al. (2017). (B) A plot of isotopic enrichment factor (ϵ) between $\delta\text{D}_{\text{CH}_4}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ ($\epsilon_{\text{methane/water}}$) versus $\Delta^{13}\text{CH}_3\text{D}$ with equilibrium curve using the Turner et al. (2021 and 2022) calibrations (Eq. (2) and Eq. (3)). Examples of thermogenic gases shown as red symbols from the Silurian Niagara Formation in the Michigan Basin, Ordovician-Cambrian formations in the southwestern Ontario (Giunta et al., 2019), and Marcellus/Utica shales in the Appalachian Basin (Wang et al., 2015). Examples of mixed microbial-thermogenic gases in the yellow symbols are from the Devonian Antrim Shale in the Michigan Basin and Silurian formations in the southwestern Ontario (Giunta et al., 2019; Stolper et al., 2015). Examples of microbial gases, shown as green symbols, are from the Santa Monica/Santa Barbara basins (Stolper et al., 2015), Northern Cascadia Margin, and Powder River Basin (Wang et al., 2015).

reservoir were slightly lower than that of gases in the deep reservoirs in the Lisbon Valley. Further studies of $\Delta^{13}\text{CH}_3\text{D}$ equilibrium and hydrogen isotopic exchange between methane and water, relative to the thermal and burial history of the Michigan Basin, and other sedimentary basins, are needed to evaluate the influence of thermal maturity versus post-genetic processes.

Very dry gas samples from the Cutler Group and Honaker Trail Formation in the Andy's Mesa and Hamilton Creek fields, in the north-eastern part of the basin, have relatively high thermal maturity with increasing $\text{CH}_4/\Sigma\text{C}_{2+}$ from 23 to 200 and consistently high $\delta^{13}\text{C}_{\text{CH}_4}$ ($-33.0 \pm 1.3\text{‰}$), $\delta^{13}\text{C}_{\text{C}_2}$ ($-28.6 \pm 2.9\text{‰}$), $\delta^{13}\text{C}_{\text{C}_3}$ ($-23.6 \pm 2.0\text{‰}$) (Figs. 3 and 4C), $\Delta^{13}\text{CH}_3\text{D}$ (2.6–3.0‰), and $\epsilon_{\text{methane/water}}$ (-102.3 to -8.2‰) (Fig. 6) values, compared to gases from the Honaker Trail Formation in the Lisbon Valley field. The high thermal maturity of gases suggests that, during maximum burial, hydrocarbons were generated from the source rock ($R_o \geq 3.05\%$) at relatively high temperatures (Fig. 2B) and migrated into the overlying formations (Fig. 9B). However, a gradual increase in dryness (from 4 to 200 $\text{CH}_4/\Sigma\text{C}_{2+}$), consistent $\delta^{13}\text{C}_{\text{CH}_4}$ values ($\sim -33\text{‰}$), and high $\Delta^{13}\text{CH}_3\text{D}$ and $\epsilon_{\text{methane/water}}$ values relative to the isotopic equilibrium curve (Fig. 7) evoke questions concerning the loss of hydrocarbons by physical processes, such as leaking or diffusion, the mixing of a dry gas with a wet gas from different sources, or post-genetic alteration of hydrocarbons by microbial activity.

Gases from the Dakota and Morrison formations (the shallowest

reservoirs in this study) in the Cisco field plot above the thermal maturity trend with relatively dry gas (14–29 of $\text{CH}_4/\Sigma\text{C}_{2+}$) and low $\delta^{13}\text{C}_{\text{CH}_4}$ values of $-44.3 \pm 2.7\text{‰}$ (Fig. 3) from mixing of moderately mature thermogenic gases with secondary microbial methane, as seen in previous studies (Zhang et al., 2009) (Fig. 3). The high $\delta^{13}\text{C}_{\text{C}_2}$ and $\delta^{13}\text{C}_{\text{C}_3}$ values ($-26.0 \pm 1.1\text{‰}$ and $-21.8 \pm 1.7\text{‰}$, respectively) in Fig. 4C indicate high thermal maturity and/or post-genetic alteration (e.g., anaerobic oxidation of hydrocarbons), as discussed below. The thermogenic gases in the Cisco field were likely sourced from the Paradox Formation shale source rocks during maximum burial (80–100 Ma; Nuccio and Condon, 1996), and later migrated into overlying reservoirs during post-Cretaceous uplift of the upthrown block along the Uncompahgre Fault (Young, 1983) approximately 50–70 Ma (Fig. 2C). Alternatively, hydrocarbons may have been sourced from thermal maturation of carbonaceous shales in the Dakota and Morrison formations (Hendel, 1961) during maximum burial (Fig. 2C; Hoffman, 2009).

The $\Delta^{13}\text{CH}_3\text{D}$ and $\epsilon_{\text{methane/water}}$ values for gases from the Dakota and Morrison formations in the Cisco field (Fig. 7) are close to or overlap with mixed microbial-thermogenic gases from the Devonian Antrim Shale of the Michigan Basin and Silurian formations of the southwestern Ontario (Giunta et al., 2019; Stolper et al., 2015) and thermogenic gas from Ordovician-Cambrian formations in southwestern Ontario (Giunta et al., 2019). The overlapping values supports the low $\Delta^{13}\text{CH}_3\text{D}$ range for mixed microbial-thermogenic gas.

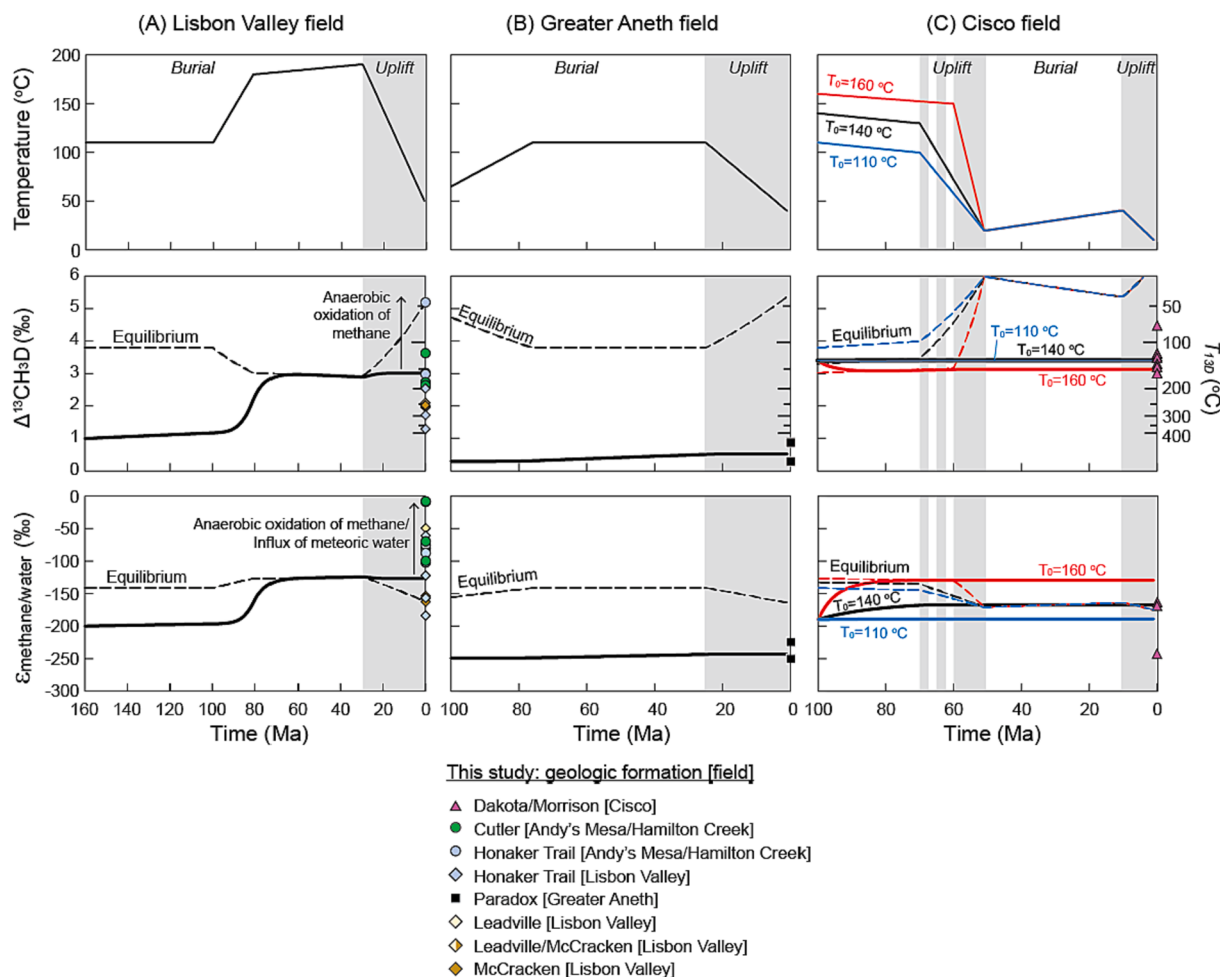


Fig. 8. Forward model results showing the time evolution of methane isotopologue compositions. (A), (B), and (C) columns are model results for source rocks in the Lisbon Valley field (northeastern side of the basin), Greater Aneth field (southwestern side of the basin), and Cisco field, respectively. The diagram at top shows the thermal history according to previous basin models. The diagram in the middle shows the time evolution of $\Delta^{13}\text{CH}_3\text{D}$ values and that expected from equilibrium (dashed line). The bottom diagram shows $\epsilon_{\text{methane/water}}$ values and that expected from equilibrium (dashed line) depending on different initial temperatures (110°C in blue, 140°C in black, and 160°C in red) at 100 Ma. The measured $\Delta^{13}\text{CH}_3\text{D}$ and $\epsilon_{\text{methane/water}}$ values in this study are plotted at 0 Ma for comparison.

5.3. Biodegradation of hydrocarbons

Methane-dominated dry, thermogenic gases in the Dakota/Morrison (Cisco field) and Cutler and Honaker Trail formations (Andy's Mesa/Hamilton Creek fields) (Fig. 3) have high $\delta^{13}\text{C}_{\text{Cn}}$ values, relative to the expected single source trend (Fig. 4A–4B), and plot above the thermogenic gas trends in both the 'Bernard plot' (Fig. 3) and the $\delta^{13}\text{C}_{\text{C}_2}$ versus $\delta^{13}\text{C}_{\text{C}_3}$ plot (Fig. 5C). Together, these isotopic shifts suggest the thermogenic gases have been altered by post-genetic biodegradation (e.g., Jenden and Kaplan, 1989; Rooney et al., 1995; Lorant et al., 1998).

Thermogenic gases in the Dakota/Morrison formations show a carbon isotopic reversal between C_3 and nC_4 (Fig. 4A) with lower $\delta^{13}\text{C}_{\text{CH}_4}$ values compared to gases in other shallow reservoirs (e.g., Cutler Group and Honaker Trail Formation in Fig. 4B). Gases from the Cutler Group and Honaker Trail Formation in the Andy's Mesa and Hamilton Creek fields also have relatively high $\delta^{13}\text{C}$ values for CH_4 compared to what is expected for a single source trend (Fig. 4B). $\delta^{13}\text{C}_{\text{C}_3}$ values for half of these gases are nearly identical to $\delta^{13}\text{C}_{\text{C}_4}$ values. The HC-25-22 and HC-30-11 samples show a carbon isotopic reversal between CH_4 and C_2 with relatively high $\delta^{13}\text{C}_{\text{CH}_4}$ and low $\delta^{13}\text{C}_{\text{C}_2}$ values. The AM-38 sample shows a carbon isotopic reversal between CH_4 and C_2 due to an elevated $\delta^{13}\text{C}_{\text{CH}_4}$ value. The MM31-42 sample from the Honaker Trail Formation in the Lisbon Valley field shows a carbon isotopic reversal between CH_4 and C_2 (Fig. 4C). The anaerobic oxidation of C_{2+} , particularly C_3 , by

microbial activity with selective consumption over other alkanes (James and Burns, 1984; Wenger et al., 2002; Martini et al., 1998, 2003, and 2008) can explain low molecular and high isotopic compositions of C_2 and C_3 (Fig. 5A and 5B) in these shallow gas reservoirs.

Anaerobic oxidation of methane (AOM) could have led to increasing disequilibrium in $\Delta^{13}\text{CH}_3\text{D}$ and $\epsilon_{\text{methane/water}}$ values for gases from the Cutler Group and Honaker Trail Formation in the Andy's Mesa and Hamilton Creek fields (Fig. 7B; Giunta et al., 2022). However, the disequilibrium in $\epsilon_{\text{methane/water}}$ values may be mainly due to different water sources in each reservoir. For example, the Cutler Group samples with the lowest $\delta\text{D}_{\text{H}_2\text{O}}$ values (−125.9‰), representing meteoric waters (Fig. 6A), exhibit the highest $\epsilon_{\text{methane/water}}$ values (−8.2 and −9.2‰) with significant disequilibrium (Fig. 7B). In contrast, reservoirs containing older, saline fluids (e.g., Leadville and McCracken formations in Lisbon Valley), with higher $\delta\text{D}_{\text{H}_2\text{O}}$ values, have lower $\epsilon_{\text{methane/water}}$ values. The deviations from the equilibrium curve in $\Delta^{13}\text{CH}_3\text{D}$ and $\epsilon_{\text{methane/water}}$ space (Fig. 7B) can serve as a new model for identification of thermogenic gases formed in the wet-gas window (plotting far below the equilibrium curve) versus biodegradation of dry-gases without generation of secondary microbial methane (plotting above the curve).

5.4. Microbial methanogenesis

The Dakota and Morrison reservoirs in the Cisco field have relatively

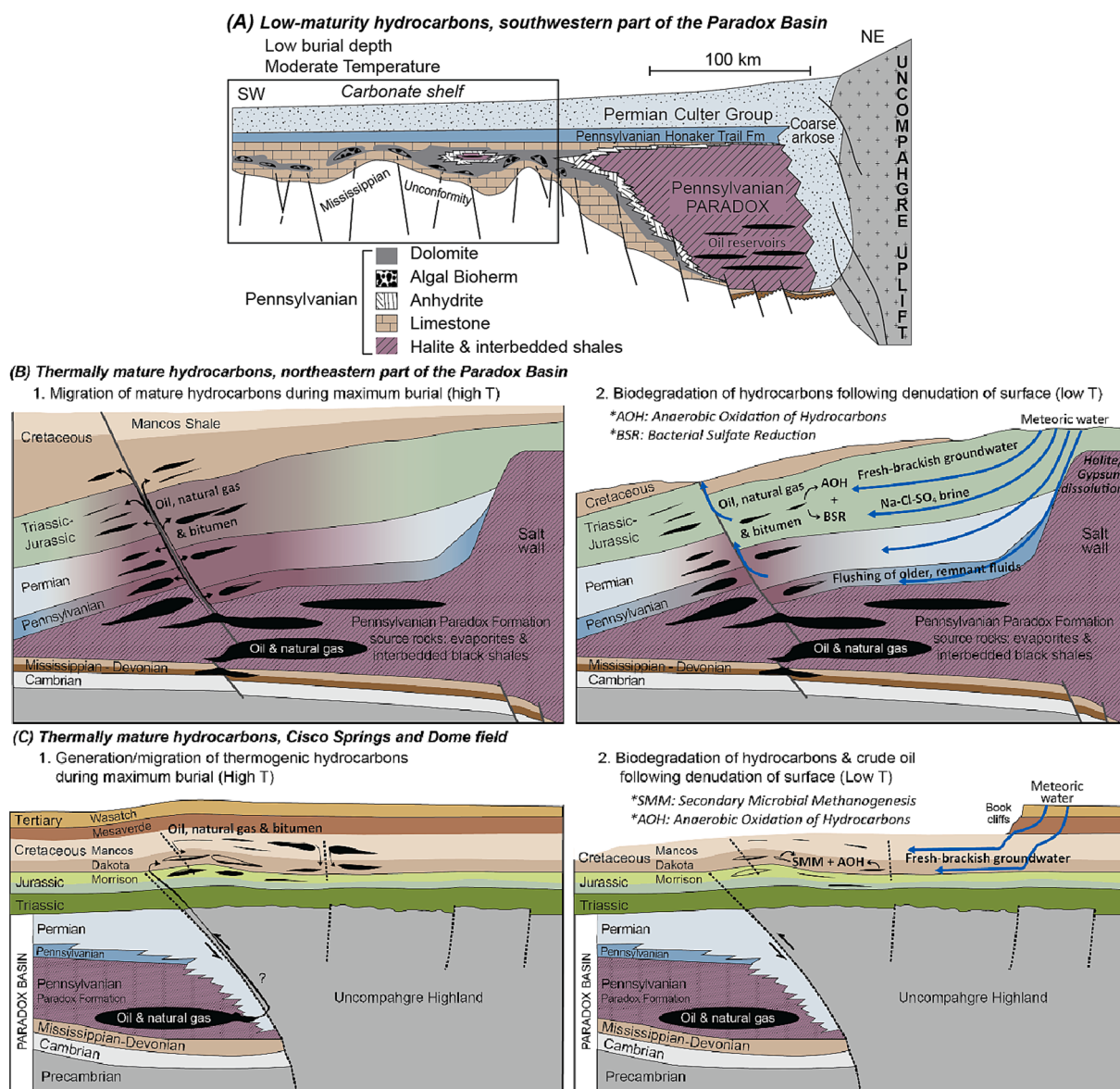


Fig. 9. (A) Schematic cross-section A-A' in Fig. 1A during the Permian, modified from Whidden et al. (2014) and Stevenson and Baars (1985). Low-maturity hydrocarbons in the black shale source rocks of the Paradox Formation at relatively shallow depth in the southwestern part of the Paradox Basin. (B) 1. Migration/Expulsion of thermally mature hydrocarbons from black shale source rocks of the Paradox Formation into overlying/underlying formations through faults at maximum burial and high temperature. 2. Following recent denudation of the Colorado Plateau (<4–10 Ma), lower temperatures and deep meteoric circulation (Kim et al., 2022b) promoted anaerobic oxidation of hydrocarbons (AOH), likely coupled to bacterial sulfate reduction (BSR) in shallow reservoirs. (C) Schematic cross-section in Cisco Springs and Dome field modified from Young (1983). 1. Generation and migration of thermogenic hydrocarbons in the Cretaceous and Jurassic sediments in the Cisco field. 2. Biodegradation of hydrocarbons and crude oil, producing secondary microbial methane (SMM) by active meteoric circulation and low temperature following uplift and the recent denudation.

low $\delta^{13}\text{C}_{\text{CH}_4}$ values ($-44.3 \pm 2.9\text{‰}$; Figs. 3 and 4A) and high CO_2 concentrations ($2.1 \pm 1.4 \text{ mol\%}$; Table 1) enriched in ^{13}C ($17.4 \pm 3.0\text{‰}$ $\delta^{13}\text{C}_{\text{CO}_2}$; Table 2), consistent with microbial methanogenesis. The δD values of CH_4 and co-produced H_2O (Fig. 6A) and $\delta^{13}\text{C}$ values of CH_4 and CO_2 (Fig. 6B) from the Dakota and Morrison formations suggest microbial methane was generated via CO_2 reduction (i.e., hydrogenotrophic methanogenesis). Deeper gases from the McCracken and Honaker Trail formations in the Lisbon Valley field appear to plot along the CO_2 reduction trend (Fig. 6A); however, $\delta^{13}\text{C}$ values of CO_2 and CH_4 in the McCracken Formation (Fig. 6B) and low CO_2 concentrations in the Honaker Trail Formation are inconsistent with microbial methanogenesis (Whiticar et al., 1986; Martini et al., 1996; 2003; Vinson et al., 2019).

As the shallow reservoirs above the Paradox Formation source rocks

were brought closer to the surface by recent (<4–10 Ma) denudation of the Colorado Plateau and reached lower temperatures ($<80^\circ\text{C}$; Nuccio and Condon, 1996; Rasmussen and Rasmussen, 2009) in contact with circulating meteoric waters (Kim et al., 2022a, 2022b; Tyne et al., 2022), microbial communities may have been re-introduced into previously sterilized reservoirs (Head et al. 2003), stimulating biodegradation of hydrocarbons and microbial methanogenesis (Fig. 9B and 9C). In particular, the further northeastern fields – Andy's Mesa, Hamilton Creek, and Cisco fields – are proximal to the Uncompahgre Uplift topographic high and regional discharge areas (e.g., Colorado River). This topography and associated hydraulic gradients promote greater meteoric fluxes and may enhance microbial activity in the shallow reservoirs (Fig. 9C) (McIntosh et al., 2023). The dissolution of gypsum by meteoric circulation around salt walls and related anticlines (Kim et al.,

2022a) could have promoted BSR and anaerobic oxidation of hydrocarbons as seen in other sedimentary basins (Adams et al., 2013; Bose et al., 2013) (Fig. 9B). Consumption of sulfate by BSR or paucity of sulfate sources, away from salt walls, may have promoted microbial methanogenesis in organic-rich reservoirs. Microbial methane in the Dakota and Morrison formations may have been generated from biodegradation of in situ carbonaceous materials, crude oil, and/or thermogenic gases (Pallasser, 2000). The extent and mechanism of microbial processes in these shallow hydrocarbon reservoirs, related to fluxes of electron acceptors (e.g., SO_4), are the focus of future work.

5.5. Alternative sources of CO_2

It is notable that the Leadville and McCracken formations contain high CO_2 concentrations (1–48 mol%; Table 1) with a narrow range of $\delta^{13}\text{C}_{\text{CO}_2}$ (−7.5 ± 0.7‰; Table 2) relative to other formations. Their $\delta^{13}\text{C}_{\text{CO}_2}$ values are within a plausible range of thermogenic gases from approximately −40 to +10‰ (Milkov and Etiope, 2018), but are also similar to mantle-sourced CO_2 in the region (−7.0 to −3.5‰; Crossey et al., 2009; Craddock et al., 2017). This suggests an influx of abiotic CO_2 into the Leadville and McCracken formations through the Precambrian basement or Cenozoic volcanic rocks (e.g., La Sal Mountains). Although there is no evidence of abiotic methane in the basal formations in either the conventional gas isotope signatures (Figs. 3 and 5C) or $\Delta^{13}\text{CH}_3\text{D}$ values (Fig. 7A). CO_2 and other crustal- or magmatic-derived gases (i.e., basement ^4He flux) have accumulated in the basal hydrostratigraphic units, sealed by overlying Paradox Formation evaporite confining units (Tyne et al., 2022). Alternatively, decarboxylation of the Leadville Formation carbonate rocks (Crossey et al., 2009) and/or microbial degradation of hydrocarbons, possibly promoted by influx of meteoric water and cooler temperatures following denudation (Kim et al., 2022b), could have contributed CO_2 .

5.6. Temporal evolution of $\Delta^{13}\text{CH}_3\text{D}$ and $\epsilon_{\text{methane/water}}$ values

Consideration of how $\Delta^{13}\text{CH}_3\text{D}$ values evolve through geologic time, in response to deep burial and higher temperatures versus uplift/denudation and cooling (Fig. 8), and exchange rates of hydrogen isotopes between methane and water, provides further insights into clumped isotope signatures of natural gas. According to Turner et al. (2022), the timescale for $\Delta^{13}\text{CH}_3\text{D}$ exchange (1/k) is ~5.4 m.y. at 160 °C and 100 m.y. at 110 °C. The Cane Creek source rocks in the northeastern part of the basin experienced the maximum temperature of up to 160 °C over 40 m.y., whereas the Ismay-Desert Creek source rocks in the southwestern part of the basin were heated to below 110 °C over 50 m.y. (Fig. 2). Thus, methane within the source rocks in the northeastern side of the basin (e.g., Lisbon Valley field) should have been thermally re-equilibrated, whereas methane in the southwestern side of the basin (e.g., Greater Aneth field) would have retained the original clumped isotope signals. Therefore, we interpret that $\Delta^{13}\text{CH}_3\text{D}$ values of 2.5 to 3.0‰ ($T_{13\text{D}} = 160$ to 200 °C; Table 2) measured in reservoirs above the Paradox Formation source rocks in the northeastern fields represent thermal equilibrium during maximum burial. Conversely, the low $\Delta^{13}\text{CH}_3\text{D}$ values measured in the Paradox Formation gases (0.3 and 0.9‰, Table 2) in the Greater Aneth field and Leadville/McCracken formation gases (1.3–2.1‰) indicate the preservation of kinetic signals from initial thermal cracking of organic matter. Note that the actual equilibrium curve for natural methane at the condition of each reservoir can differ from the gas-phase equilibrium curve predicted by theory and calibrated in the laboratory (Xie et al., 2021).

$\Delta^{13}\text{CH}_3\text{D}$ and $\epsilon_{\text{methane/water}}$ equilibrium is achieved at temperatures above 160 °C in the model, according to Eq. (2) and Eq. (3). Thus, once methane is equilibrated with $\Delta^{13}\text{CH}_3\text{D}$ and hydrogen isotopes of water, the final $\Delta^{13}\text{CH}_3\text{D}$ and $\epsilon_{\text{methane/water}}$ values reflect the environmental conditions of the last equilibrium, regardless of any choice of initial $\Delta^{13}\text{CH}_3\text{D}$ and $\epsilon_{\text{methane/water}}$ values. In the model of the source rocks

(Cane Creek members of the Paradox Formation) in the Lisbon Valley field, the mean values of measured $\Delta^{13}\text{CH}_3\text{D}$ and $\epsilon_{\text{methane/water}}$ values were used as initial values. The thermally equilibrated $\Delta^{13}\text{CH}_3\text{D}$ (Fig. 8A) is consistent with the high thermal maturities of the source rocks (Fig. 1B) and hydrocarbons remaining in the reservoirs above and below the Paradox Formation (Figs. 3 and 5C). This observation suggests that thermogenic gases containing thermally equilibrated $\Delta^{13}\text{CH}_3\text{D}$ represent hydrocarbons from a source that reached high thermal maturity.

The mature thermogenic gases, with $\Delta^{13}\text{CH}_3\text{D}$ values corresponding to equilibration at 160–170 °C over ~50 m.y. (30–80 Ma; Fig. 8A), would have been expelled into the overlying Honaker Trail Formation reservoirs during maximum burial, along faults (Fig. 9B). The relatively early generated, low to moderate maturity thermogenic gases that migrated during the beginning stage of burial (80–100 Ma) into the underlying Leadville/McCracken formations, would have not been equilibrated with respect to $\Delta^{13}\text{CH}_3\text{D}$ with unreasonably high $T_{13\text{D}}$ values (247–374 °C) compared to the burial/thermal history of the basal formations (<200 °C; Fig. 2A). Although the modeled $\Delta^{13}\text{CH}_3\text{D}$ -based temperature at equilibrium slightly decreased from 170 to 160 °C between 30 Ma to the present due to cooling effects (by uplift and erosion) (Fig. 8A), $\Delta^{13}\text{CH}_3\text{D}$ values still closely reflect the equilibrium temperature of the last deep burial.

The modeled $\epsilon_{\text{methane/water}}$ values for the Lisbon Valley field, based on the thermal histories, suggest methane resided at depth under relatively high temperatures (≥ 160 °C) for enough time (e.g., at least for 40 m.y. between 30 and 70 Ma; Fig. 8A) for hydrogen isotope exchange of hydrocarbons with formation water (Koepp, 1978; Sessions et al., 2004; Xie et al., 2020 & 2021). It is also possible that methane has (re)equilibrated with some other sources of hydrogen such as H_2 (0.5 mol% from the Leadville/McCracken formations; Table 1) and other hydrogen-bearing compounds (e.g., on clay mineral surfaces) or that the hydrogen (D/H) exchange responsible for the (re)equilibrium has been accelerated by interaction with catalytic materials, such as metal oxide and organometallic complexes (Sattler, 2018; Giunta et al., 2021).

If we assume the thermal history of the Cutler Group and Honaker Trail Formation in the Andy's Mesa and Hamilton Creek fields is similar to the nearby Lisbon Valley (Fig. 2A), deep burial of the source rocks in the northeastern part of the basin above 160 °C would have led to $\Delta^{13}\text{CH}_3\text{D}$ equilibrium (Fig. 8A) with measured $T_{13\text{D}}$ values of 160–195 °C. Later AOM, following denudation, would have led to disequilibrium in $\Delta^{13}\text{CH}_3\text{D}$ and hydrogen isotopes between CH_4 and H_2O , as observed at present. There might also have not been enough time for recent recharge waters, with lower $\delta\text{D}_{\text{H}_2\text{O}}$ values, to have equilibrated with methane (Kim et al., 2022b).

The high $\Delta^{13}\text{CH}_3\text{D}$ value (5.2‰) of one sample (HC12-13) from the Honaker Trail Formation in the Hamilton Creek field, plotting in the mixed microbial-thermogenic gas field (Fig. 7), is identical to the modeled $\Delta^{13}\text{CH}_3\text{D}$ value in equilibrium at present temperature (Fig. 8A). This sample could have been affected by AOM or mixed with (secondary) microbial methane at low apparent temperatures ($T_{13\text{D}}$ of 47 °C) following recent denudation. AOM can (re)equilibrate methane (Fig. 8A) through exchange catalysis during enzymatic back reactions (Ash et al., 2019) under low temperature (<70 °C) conditions. Interestingly, the bulk carbon isotopic composition of this sample shows no evidence of anaerobic oxidation (e.g., carbon isotopic reversal between CH_4 and C_2), indicating $\Delta^{13}\text{CH}_3\text{D}$ may be a more sensitive tracer for microbial carbon cycling, as recently suggested by Giunta et al. (2022). Alternatively, the sample's $\Delta^{13}\text{CH}_3\text{D}$ value plots within the range of abiotic methane (Wang et al., 2015; Young et al., 2017; Douglas et al., 2017), and its $\delta^{13}\text{C}_{\text{CO}_2}$ values (−7.1 ± 0.2‰; Table 2) are similar to mantle-sourced CO_2 in the region (Crossey et al., 2009; Craddock et al., 2017). As mentioned above, characterization of microbial communities in these hydrocarbon reservoirs is needed to further interpret methane isotopologue signatures.

In the models for the Greater Aneth field (Fig. 8B), because of the

lack of initial $\Delta^{13}\text{CH}_3\text{D}$ and $\varepsilon_{\text{methane/water}}$ data at 100 Ma, initial values were assumed to be similar to measured values of gases present today in the source rocks ($\Delta^{13}\text{CH}_3\text{D}$ of 0.3‰ and $\varepsilon_{\text{methane/water}}$ of −250‰). The temperature during maximum burial ($\leq 110^\circ\text{C}$) was too low to equilibrate $\Delta^{13}\text{CH}_3\text{D}$ and $\varepsilon_{\text{methane/water}}$ in the source rocks (i.e., Ismay-Desert Creek members of the Paradox Formation) (Fig. 8B). The modeled $\Delta^{13}\text{CH}_3\text{D}$ and $\varepsilon_{\text{methane/water}}$ values slightly increased during burial (25–80 Ma) without reaching equilibrium and then maintained their values after cooling. The observed disequilibrium of $\Delta^{13}\text{CH}_3\text{D}$ and hydrogen isotopes between methane and water (Fig. 8B) supports the low thermal maturity of hydrocarbons in the Greater Aneth field.

In the three models for source rocks in the Cisco field (Fig. 8C), the average measured $\Delta^{13}\text{CH}_3\text{D}$ (3.4‰) and $\varepsilon_{\text{methane/water}}$ (−190‰) values were used as initial values at 100 Ma. The forward model results particularly starting 140°C , based on the thermal and burial history of the shallow source rocks in the field (Figs. 2C and 9C), align with measured $\Delta^{13}\text{CH}_3\text{D}$ and $\varepsilon_{\text{methane/water}}$ values. This observation suggests that high $\Delta^{13}\text{CH}_3\text{D}$ values, corresponding to the low range of $T_{13\text{D}}$ values ($133 \pm 27^\circ\text{C}$), can be explained by multiple mechanisms for methane generation. Thermogenic methane first equilibrated with $\Delta^{13}\text{CH}_3\text{D}$ under high temperature ($130\text{--}140^\circ\text{C}$) conditions around 60–100 Ma, while secondary microbial methane was generated more recently (around 10–50 Ma), possibly from oil biodegradation, and equilibrated with δD of water under lower temperatures ($20\text{--}40^\circ\text{C}$) (Figs. 7B, 8C, and 9C) (Head et al., 2003; Wang et al., 2015). The new equilibrium model, based on the hydrogen isotope exchange rate and thermal history, helps constrain methane isotopologue signatures and the temporal evolution of hydrocarbons in the subsurface.

6. Conclusions

Results of this study highlight the applicability of clumped isotopologues ($\Delta^{13}\text{CH}_3\text{D}$) to illuminate veiled isotopic signals of microbial methane, obfuscated by the presence of thermogenic gas and anaerobic oxidation of hydrocarbons. Furthermore, this study constructed a new equilibrium model based on the hydrogen isotope exchange rate between CH_4 and H_2O and basin thermal history to support the temporal evolution of $\Delta^{13}\text{CH}_3\text{D}$ values – a new approach in hydrocarbon geochemistry. The integrated observation and modeling results, including conventional and clumped isotopes, provides a better understanding of the origins and fate of hydrocarbons in dynamic and complex shallow crustal environments.

The pervasive presence of thermogenic gases, in reservoirs above and below the Paradox Formation shale source rocks, in the Paradox Basin is consistent with the basin's deep burial history. Biodegradation of hydrocarbons and presence of microbial methane points to recent denudation and meteoric circulation enhancing microbial activity in shallow reservoirs.

[1] Low-maturity thermogenic gases are present along the southwestern margin of the basin that was never deeply buried. The low $\Delta^{13}\text{CH}_3\text{D}$ values of these thermogenic gases suggest methane retained its disequilibrium signal from initial generation.

[2] Low to moderate maturity thermogenic gases were generated in Paradox Formation source rocks, interbedded with evaporites, during early burial of the northeastern part of the basin, and expelled into underlying reservoirs, trapped by the salt walls. As the basin continued to subside, methane in the underlying reservoirs was isolated from the source rocks and thermally disequilibrated with respect to $\Delta^{13}\text{CH}_3\text{D}$. During maximum burial, higher maturity hydrocarbons were generated in the Paradox Formation source rocks and expelled into overlying reservoirs, and later biodegraded via anaerobic oxidation of hydrocarbons, especially ethane and propane. The biodegradation of hydrocarbons was likely enhanced by recent denudation of the Colorado Plateau in the last ~4–10 Ma and coupled to BSR with abundant sulfate from meteoric circulation and

gypsum dissolution around salt walls. Microbial methane, isotopically equilibrated with water, was also generated in the shallowest oil/gas reservoirs and mixed with thermogenic gases.

[3] The $\Delta^{13}\text{CH}_3\text{D}$ and hydrogen isotopic equilibrium results in this study provide new insights for a dichotomy of disequilibrium between low-maturity thermogenic gases and biodegraded thermally-mature thermogenic gases. Study results also extend the field of $\Delta^{13}\text{CH}_3\text{D}$ values of thermogenic gases. Together with more traditional molecular and isotopic gas composition, $\Delta^{13}\text{CH}_3\text{D}$ is a sensitive tracer for illuminating the history of carbon cycling in sedimentary basins from initial generation of hydrocarbons, maximum burial and thermal equilibration, and post-genetic biodegradation, following denudation and meteoric circulation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Research data associated with the forward models for $\Delta^{13}\text{CH}_3\text{D}$ equilibration are available in the Supplementary Material and include time, temperature of source rocks, equilibrium temperature based on modeled $\Delta^{13}\text{CH}_3\text{D}$, modeled $\Delta^{13}\text{CH}_3\text{D}$ values, $\Delta^{13}\text{CH}_3\text{D}$ values expected from equilibrium, modeled $\varepsilon_{\text{methane/water}}$ values, and $\varepsilon_{\text{methane/water}}$ values expected from equilibrium for Lisbon Valley, Greater Aneth, and Cisco fields. The dataset of the Cisco field consists of three different results depending on the initial temperatures of source rocks ($T_0 = 160, 140$, and 110°C). Supplementary material to this article can be found online at <https://doi.org/10.1016/j.gca.2023.10.017>.

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