Reply to Anonymous discussion author regarding Comments on "Ideas and perspectives: is shale gas a major driver of recent increase in global atmospheric methane?" by Robert Howarth (2019)

By Michael D. Lewan, USGS Denver CO (mlewan@USGS.gov)
Michael Whiticar, University of Victoria, CA (whiticar@uvic.ca)
Alexei Milkov, Colorado School of Mines CO (amilkov@mines.ed)

Considering the high radiative forcing of atmospheric methane, it is important to reliably identify and quantifying the sources and sinks to understand the methane budget. The challenge is further emphasized by the renewed increase in net methane accumulation in the atmosphere since 2007, and identifying the cause(s) for the changes. The assignment of representative stable isotope ratios, e.g., $\delta^{13}CH_4$, to the various methane sources and isotope fractionation by sinks is an integral part of this methane budget process. If we are to effect real reductions in methane emissions, then accurately quantifying the flux strengths and signatures is a requisite need.

The Howarth (2019) paper, which has precipitated this discussion, assigned $\delta^{13}CH_4$ values of shale gas ('SG'), conventional natural gas (termed 'CG'), gas associated with oil production, gas associated with coal production, and biogenic (microbial, 'B') and biomass burning (pyrogenic) emitting to the atmosphere (Howarth's Table 1). We argue that the $\delta^{13}CH_4$ values for SG chosen by Howarth (2019) are demonstrably not representative. As these values cascade through the calculated mass balance in Howarth (2019), this leads to erroneous conclusions. The selection of more representative $\delta^{13}CH_4$ values for fossil fuels and the attendant supporting information is provided and discussed in Lewan (2020). This paper responds directly to the comments in the discussion by the Anonymous Referee #1 (AR1, 2020).

The issue revolves largely around the selection of the $\delta^{13}CH_4$ values for shale gas (SG). First, Lewan (2020) commented that there is substantial overlap in the range of $\delta^{13}CH_4$ values for shale methane and conventional methane. This ineffectiveness of $\delta^{13}CH_4$ values to unambiguously differentiate sources has been stated by numerous authors, e.g., Nisbet et al. (2016), Turner et al. (2019). The $\delta^{13}CH_4$ overlap and lack of discrimination between SG and CG has been clearly shown by the extensive global natural gas database from Milkov et al. (2020). The latter paper further shows that the range in $\delta^{13}CH_4$ values for SG and CG is large (46.7 ‰ and 88.2 ‰, respectively). However, their mean $\delta^{13}CH_4$ values for SG and CG are respectively -41.1 ‰ and -42.8 ‰, which are notably different from Howarth (2019) values of -46.9 ‰ and -44 ‰, respectively. Although AR1 (2020) refers to these concerns by Lewan 2019 as 'nit picking', having representative $\delta^{13}CH_4$ values is important as we will demonstrate.

Lewan (2019) employed the same rational and mathematical constructs as in Howarth (2019), but with $\delta^{13}CH_4$ values deemed more representative and appropriate for shale gas. As a result, the revised calculation shows that shale gas is not the main driver of recent increases in global methane atmosphere. Whereas opposed to percentages, actual magnitudes are very important with shale gas methane being reduced by 2.6 Tg/year and all other fossil-fuel methane reduced by 1.5 Tg/year for a total fossil fuel methane reduction of 4.1 Tg/year with a calculated biogenic methane increase of 4.1 Tg/year, which is 14.4% of the 28.4 Tg /year global increase determined by Worden et al. (

2017). As noted by AR1 (2020), these more representative isotopic values change the conclusion prescribed by Howarth (2019).

The definition of shale gas used by Howarth (2019), as produced methane and associated gases released from shale rock by high volume hydraulic fracturing, is not universally accepted. In some instances, hydraulic fracturing is not a requirement and that shale gas is termed as natural gas produced from shales (e.g., Curtis, 2002; Jarvie, 2012). Regardless, of which definition is preferred, the database compiled by Lewan (2019, Table 1) complies with the definition of Howarth (2019), albeit some of the AR1 (2020)'s and those of Howarth (2019) examples are not consistent with the definition of Howarth (2019).

The AR1 (2020) uses the study by Muehlenbachs and Arismendi (2019) in the Western Canada Sedimentary Basin (WCSB) as evidence for the isotopically light shale gas methane emissions. In the abstract of this study, the gases reported are from surface casing vent flow and ground migration gases that have ^{13}C-depleted (isotopically 'light') $\delta^{13}CH_4$ values (-58.4 and -57.3‰, respectively) suggesting a major microbial (biogenic) methane component. According to the authors, these emissions originate mostly from formations shallower than the shale gas horizons, which is indicative of migrated gases not related to the shale gas in underlying targeted shale intervals. It is common for groundwaters, especially under anaerobic conditions, to contain microbial methane generated via methanogenesis. In addition to $\delta^{13}CH_4$ values, there is no supporting evidence presented by AR1 (2020) demonstrating that these gases were originally thermogenic shale gases. Therefore, it is tenuous solely on the Muehlenbachs and Arismendi (2019) study to state that shale gas is more ^{13}C-depleted than conventional gas. In fact, stray gas and ground water gases are typically from microbial sources with ^{13}C-depleted $\delta^{13}CH_4$ values (e.g., Jackson et al., 2013; and Botnar et al., 2018; and Kulongoski, et al., 2018). These results do not provide unequivocal evidence that shale gas development is responsible for the increase in atmospheric methane emissions over the past decade.

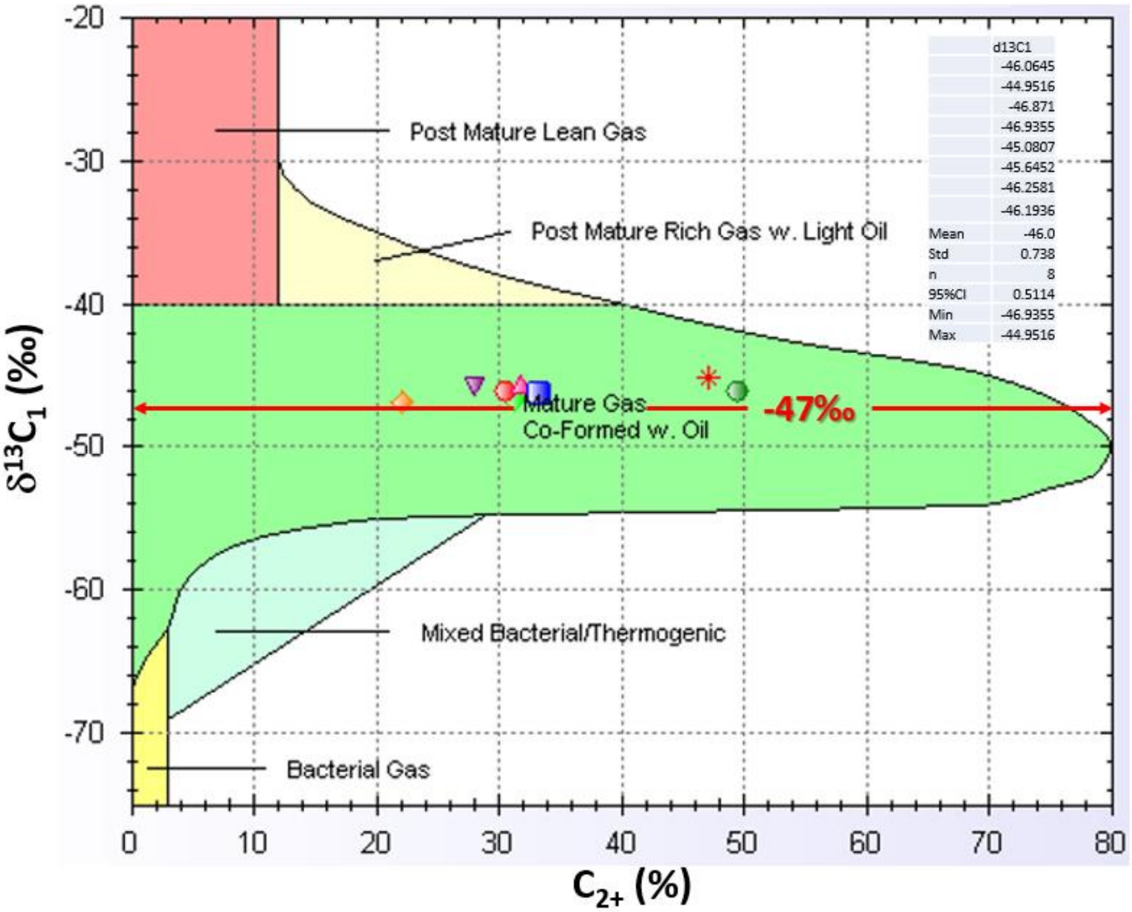
Specific: detailed responses:
Lines 10-12: The recent paper by Milkov et al. (2020) that compiles over 1,656 global SG samples and 12,416 CG samples is considered to be more robust than the 43 selected SG samples used by Howarth (2019). This extensive data base by Milkov is now included in the revised Comment paper.

Lines 21-24:The Comment by Lewan (2020) should have included the work and conclusions by Worden et al. (2017). The work by Worden et al. (2017) is cited by Lewan (2019) but within the context of balancing increases of 28.4 Tg/yr of methane emissions as used in Equation 1 presented by Howarth (2019). Similarly, the failure to cite Turner et al. (2016) was simply an oversight.

Lines 26-31: The comment by Lewan (2019) was intended to gain clarity on gaining an explanation as to why the Howarth (2019) did not utilize the Sherwood et al. (2017) database and eliminate the entries he did not consider to be shale gas. Howarth (2019) or AR1 (2020) to evaluate the $\delta^{13}CH_4$ shale gas from horizontal wells versus so called conventional gas from vertical wells would have provided a great comparison for Howarth (2019) to use in his subject paper to document their claims. A similar concern arises with Howarth's (2019) argument that $\delta^{13}CH_4$ values of shale gas are different from migrated conventional gas.

Lewan (2019) consciously did not include the data by Tilley and Muehlenbachs (2013) to ensure omission of migrated CG from his data set and only used proper shale gas entries to determine a mean value. Certainly, the use of datasets requires due diligence and scrutiny to ascertain their reliability. If the data selection is flawed, then it is important to determine how this impacts the conclusions. Yes, an investigator does need to go back through a data set to make determinations as to whether the $\delta^{13}CH_4$ values are from shale gas or conventional gas. And yes, this may require going back to the original papers to establish their type. This is the best practice before condemning other large data bases as being unusable. So, if some of the data in a data set were as stated by Howarth (2019) unreliable, then clear examples should be shown how the inclusion of these questionable values impact the outcome.

Lines 34-35: Lewan (2019) used the strict definition by Howarth (2019) of shale gas and used the term "proper" to emphasize the gases that are produced from shale. The Bakken gasses associated with oil production in the Bakken Shale Formation are actually produced from clastic and carbonate reservoirs in the middle of the Bakken Shale Formation and not from the over or underlying shale lithologies. In this case, the gases are migrated and *senso stricto* not shale gases because of their migration according to the definition prescribed by Howarth (2019). Therefore, the oil associated gases in the Bakken should not be included in the mean of shale gas $\delta^{13}CH_4$ values. The AR1 (2020) asserts that Lewan (2019) was mistaken in stating that all of the Bakken gas isotope values plotted by Schoell and LeFever (2011) are heavier than -47‰. As shown in Figure 1 from Schoell and Lever (2011), the Bakken gases are heavier than -47‰. The values inserted in this plot are taken from Schoell and Lever (2011) and not from Sherwood et al. (2017) as suggested by AR1 (2020). It should be noted that Figure 1 is from a different article than cited by Howarth (2019), i.e., Schoell et al. (2011). But the plots in this latter paper have the same gases with $\delta^{13}CH_4$ values more ^{13}C-enriched ('heavier') than -47.0 ‰. Thus, the proposed mean for the Bakken gases by Howarth (2019) is not possible. The $\delta^{13}CH_4$ values in Schoell et al. (2011) are also heavier than -47 ‰ with values between -44.97 ‰ and -46.92 ‰ and a mean of -46.0 ‰, similar to Figure 1. Although the difference in the choice of a mean of -47‰ by Howarth (2019) is not consequential in the overall atmospheric mass balance, it clarifies the difference in Bakken values by Howarth and Lewan in Table 1.



	d13C1
	-46.0645
	-44.9516
	-46.871
	-46.9355
	-45.0807
	-45.6452
	-46.2581
	-46.1936
Mean	-46.0
Std	0.738
n	8
95%CI	0.5114
Min	-46.9355
Max	-44.9516

Figure 1. Plot presented by Schoell and LeFever (2011) showing composition and **$\delta^{13}CH_4$** ***values for Associated gases produced with oil from the Bakken Shale.***

Lines 46 – 59: The AR1 (2020) correctly notes that Botner et al. (2018) obtained their conventional and shale gases from production wells, although the actual well data or statistics were not presented in the paper. A personal communication with Botner (April 17, 2020) confirms these two values represent single gases collected from a producing SG and CG gas wells in Carroll County and are not a statistical mean of several produced gases from the Utica. As stated by Lewan (2019) and Botner et al. (2018), the gas representing the CG is from a residential groundwater well that drilled into a conventional gas well. The SG sample was taken downwind from a shale gas well and corrected for atmospheric air. The thermal maturity of the shales in these two wells is not given, but thermal maturity maps indicate that Carroll County (Riley, 2016) straddles a range of thermal maturities from oil generation (0.6-0.8 %VR_o) through wet gas (0.8-1.0%VR_o). This can have a notable effect on the $\delta^{13}CH_4$ values depending on the specific location of the wells and explain the differences in values without invoking oxidation during migration.

AR1 (2020) correctly states that the data set of Burruss and Laughery (2010) does not distinguish between shale and conventional gases. However, Burruss and Laughery (2010) do identify a gas produced from the Utica, which is considered a proper shale gas in Table 1 of Lewan (2019). The other gases are collectively grouped in the migrated gas category, but may include some shale gases. The posted Proper Utica shale gas $\delta^{13}CH_4$ value of -27.0‰ is much heavier than the -47.3‰

used by Howarth (2019). Milkov et al. (2020) also posted a heavier mean $\delta^{13}CH_4$ of -31.8‰ for the Utica based on 4 samples. It is worth noting that the total mean reported in Table 1 of Lewan (2019) for proper SG does not include any $\delta^{13}CH_4$ values from Burruss and Laughery (2010) with the exception of the one sample produced from the Utica. Because the Burruss and Laughery (2010) data cannot be differentiated as SG or CG, 39 of their samples are classified as migrated shale gas in Table 1.

Lines 61-65:
It remains difficult to understand the rational of AR1 (2020) to represent the $\delta^{13}CH_4$ for the Barnett Shale with atmospheric samples, which are known to be admixed with microbial gas component, instead of using the values of Zumberge et al. (2012) obtained from gases produced directly from the Barnett Shale. The relationship between the atmospheric gas samples from Townsend et al. (2015) to the produced samples reported by Zumberge et al. (2012) is not established. AR1 (2020) states that the Rodriquez and Philp (2010) data are from horizontal and vertical wells with no distinction between the two, which is correct. However, it is critical to state that these vertical and horizontal wells are all producing gas from the Barnett Shale, which makes them shale gas regardless of the drilling direction. It is useful to note that it is convention to denote horizontal wells with an upper-case **H** in the suffix of a well number. Consequently, 89% of the Zumberge et al. (2012) gases or shale gases are from horizontal wells. The Zumberge et al. (2012) data set for the Barnett Shale, using only gases from horizontal wells gives essentially the same statistical values as those in Table 1 with a mean $\delta^{13}CH_4$ of -41.0 ± 2.4 ‰. Interestingly, the remaining 18 Barnett Shale gases from vertical wells have a mean $\delta^{13}CH_4$ of -41.2 ± 3.1 ‰, which is indistinguishable from horizontally drilled gases. Therefore, the values given in Table 1 of Lewan (2019) to determine a mean shale gas $\delta^{13}CH_4$ remain reasonable and representative of shale gas from the Barnett Shale, and are isotopically heavier than -46.5‰ used by Howarth (2019).

Shale gas can be produced from both vertical and horizontal wells, in contrast to the positions of Howarth (2019) and AR1 (2020). For example, Devonian shale gas has been produced in New York State from vertical unstimulated wells since 1821 (Curtis, 2002). Fayettville Shale data set (Zumberge et al., 2012) has a mean $\delta^{13}CH_4$ of -37.4 ± 5.4 ‰, which is the best mean $\delta^{13}CH_4$ for Fayetteville proper (horizontal wells) gases in Table 1 of Lewan (2020). This is statistically not significantly different than the mean $\delta^{13}CH_4$ of -38.9 ±1.2 ‰ for the vertical gas wells, or for the mean $\delta^{13}CH_4$ of -38.2 ±1.5 ‰ given in Lewan (2020) Table 1.

AR1 (2020) challenges, but without any supporting information, the use of the mud gas logging (MGL) isotope values for the Marcellus Shale (e.g., Baldassare et al., 2014). MGL is a well-established, industry technology, (e.g., McKinney et al 2007, Berman et al., 2002, Ellis et al., 1999, 2003, Stankiewicz, et al., 2007) that strongly supports the inclusion of MGL $\delta^{13}CH_4$ data, including the Marcellus Shale. The AR1 (2020) argument using Dawson and Murray (2011) does not necessarily pertain to shale gas methane. Although it is an extended abstract, it includes figures with plotted data. Figure 2, shows an excellent one-to-one correlation between $\delta^{13}CH_4$ values of bottom-hole gas, i.e., produced gas, and MGL gas. Whether these plotted gases are shale gas or conventional gas is not pertinent; it does demonstrate that MGL gas signatures accurately reflect that of produced gas.

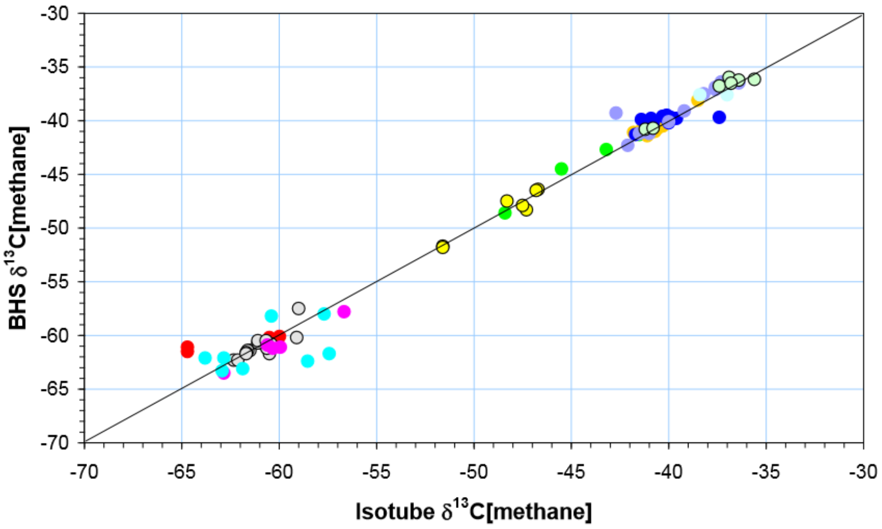


Figure 2. Comparison of $\delta^{13}CH_4$ obtained from mud gas samples (isotubes) versus bottom hole gas samples (95 samples, from Dawson and Murray, 2011).

For clarity, Lewan (2019) did not include in the proper mean $\delta^{13}CH_4$ the gases reported by Baldassare et al. (2014) that have potentially migrated, which is in accordance with the definition of SG by Howarth (2019).

Lines 88-90:

Howarth (2019) uses a shale gas (SG) mean $\delta^{13}CH_4$ of -46.9 ‰ and a mean $\delta^{13}CH_4$ of -44.0 ‰ (using a flux weighted $\delta^{13}CH_4$ atmospheric input of -53.5 ‰ and an isotope difference, DFF-A of -9.5 ‰). Howarth (2019) explains this 2.9 ‰ offset between the SG and CG to be due to methane oxidation during migration. Although this difference deminishes using the more representative shale gas (SG) mean $\delta^{13}CH_4$ of -44 ‰ (e.g., Milkov et al., 2020), the notion of extensive methanotrophy for conventional gas presented by Howarth (2019) has its own attendant issues. Aerobic (AeOM) and anaerobic (AOM) microbial methane oxidation are both well understood mechanisms in natural systems, e.g., Claypool and Kaplan (1974), Martens and Berner (1974), Reeburgh (1976), King (1992), Hanson and Hanson (1996), Lindstrom (2006) and Hinrichs and Boetius (2002). It is a pervasive feature in many shallow sediments, soils and water columns. In contrast, extensive methane oxidation in subsurface sedimentary systems, such as proposed by Howarth (2019) is essentially undocumented as evidenced by the lack of supporting references in the paper. However, secondary effects that create mixtures in reservoirs are frequently observed. This includes the addition of microbial methane or the commingling of abiotic or higher maturity methane to the conventional thermogenic gases (e.g., Golding et al., 2013 Hao and Zou, 2013, cited in Howarth, 2019). These additions can shift the natural gas to isotopically ^{12}C-enriched (microbial methane) or ^{13}C-enriched values (higher maturity gas, e.g., Stahl and Carey, 1975, James, 1983, Faber, 1987, Cramer et al., 1998, Tang et al., 2000).

AeOM and AOM are well studied mechanisms and are associated with predictable kinetic isotope effects, such that AeOM and AOM consume $^{12}C^1H_4$ at a greater rate than the heavier isotopologues $^{13}CH_4$, $^{12}C^1H_3{}^2H$, etc. (e.g., Lebedew et al., 1969, Zyakun et al., 1979, Coleman et al., 1981, Whiticar and Faber, 1986, Kinnaman et al., 2007). The range of ^{13}C enrichment for the residual methane (ε_C) due to methane oxidation based on empirical measurements and incubations is around 5 – 10, but ranges up to 31 (e.g., Coleman et al., 1981, Whiticar and Faber, 1986, Alperin et al., 1988, Kinnaman et al., 2007, Feisthauer et al., 2011, Penger et al., 2012, Rasigraf et al., 2012).

Using the classical Rayleigh fractional distillation equation, we can hypothetically calculate for the Howarth (2019) paper the fraction of methane in the conventional gas (CG) that must be consumed by microbes in order to shift the CG mean $\delta^{13}CH_4$ from -46.9 ‰ to -44.0 ‰. Assuming typical carbon isotope enrichment factors (ε_C) values of 5 and 10 (Whiticar, 1999), and using the initial (δ_o) and final (δ_t) $\delta^{13}CH_4$ values of -46.9 ‰ to -44.0 ‰, respectively (from Howarth, 2019), in Equation X from Mariotti, et al., 1981:

$$\varepsilon_C = 10^3 \ln \frac{10^{-3}\delta_t + 1}{10^{-3}\delta_o + 1} / \ln f, \qquad \text{(X)}$$

we can calculate 1-f, i.e., the fraction of methane from conventional gas consumed by AeOM or AOM postulated by Howarth (2019) during transport from source rock to reservoir. The lower ε_C value of 5 calculates a 45 % loss and ε_C of 10 is 26 % loss of methane. In other words, there would be extensive losses of CG methane required if microbial oxidation were operative, as suggested by Howarth (2019). This raises the requirement of the sufficient availability of suitable terminal electron acceptors to support AeOM or AOM.

Most subsurface oil and gas systems are anaerobic, so dissolved oxygen, nitrate, etc., are very restricted for AeOM. Dissolved sulfate, a possible AOM choice (e.g., Hoehler et al., 1994, Boetius et al., 2000, Orphan et al., 2001) is not universally available in the subsurface. Importantly, the result of AOM with sulfate is the formation of H_2S. If 25 – 50 % of natural gas methane is consumed by AOM, consistent with the suggestion in Howarth (2019), then we must expect that most, if not all, conventional gases must be sour, i.e., contain high proportions of H_2S, which they do not (e.g., Gong et al., 2014). Worldwide, roughly 25 – 30 % of wells contain H_2S (e.g., Burgers et al., 2011). A high proportion of these H_2S -bearing gas fields are the result of thermochemical sulfate reduction (TSR) and the thermal decomposition of organic matter (TDOM), i.e., oil, bitumen, and kerogen, rather than bacterial sulfate reduction (BSR) associated with methanotrophy (e.g., Orr, 1977, Machel et al., 1995, Worden et al., 1995). TSR and TDOM are higher temperature reactions, that are at or above the typical bacterial pasteurization temperature (~80 °C; Larter et al., 2006)) for BSR activity.

The persistence of H_2S in some CG settings, precludes the argument that quantitative sulfide precipitation (e.g., pyrite) could possibly explain for the absence of H_2S formed by CG methane oxidation. Furthermore, sulfur products formed from BSR and TSR have long been recognized to generally have diagnostically different $\delta^{34}S$ signatures (Harrison and Thode, 1957, Thode et al., 1958, Orr, 1974, Krouse et al., 1988, Cai et al., 2010).

The postulate by Howarth (2019) of ubiquitous microbial methane oxidation of conventional gas is also difficult to reconcile when the associated changes in gas wetness are considered. If AOM or AeOM remove methane, then the residual higher hydrocarbons (e.g., ethane, propane, butane) become preferentially enriched relative to methane. This increase in gas ‘wetness’ can be represented by the widely used Bernard parameter (Bernard, 1978) as in Eq. Y.

$$CH_4/(C_2H_6 + C_3H_8) \text{ (mol\% basis).} \tag{Y}$$

It is possible with Eq Z (Whiticar and Faber, 1986) to calculate the expected shift in gas composition due to methane oxidation, i.e., shift in the Bernard parameter to wetter values.

$$\alpha_C = \frac{lnB_t - lnB_o}{(lnB_t - lnB_o) + [(\delta_t - \delta_o)/10^3]}, \tag{Z}$$

Taking the Howarth (2019) $\delta^{13}CH_4$ values for SG (δ_o = -46.9 ‰) and CG (δ_t = -44.0 ‰) and reasonable values of ε_C of 5 and 10 (α_C of 1.005 and 1.010) for carbon isotope fractionation due to methane oxidation, and a Bernard Ratio of unaltered shale gas (SG) of 10, the Bernard Ratio of the oxidized gas (CG) would shift to 5.6 and 7.5, respectively. Setting the Bernard Ratio of SG to be 20 then the shift for CG would be to 11 and 15, respectively. Not only are these calculated shifts dramatic increases in gas wetness, but are contrary to the $\delta^{13}CH_4$–Bernard Ratio relationships observed for natural gases. As seen in Figure 3, the predominant trajectory is that the natural gases become dryer (higher Bernard Ratio) with increasing ^{13}C-enrichment of $\delta^{13}CH_4$. This trajectory is that expected for gases derived from organic matter at increasingly high maturity (e.g., Stahl, 1973, Schoell, 1980, Whiticar, 1994) and not microbial methane oxidation (Figure 3).

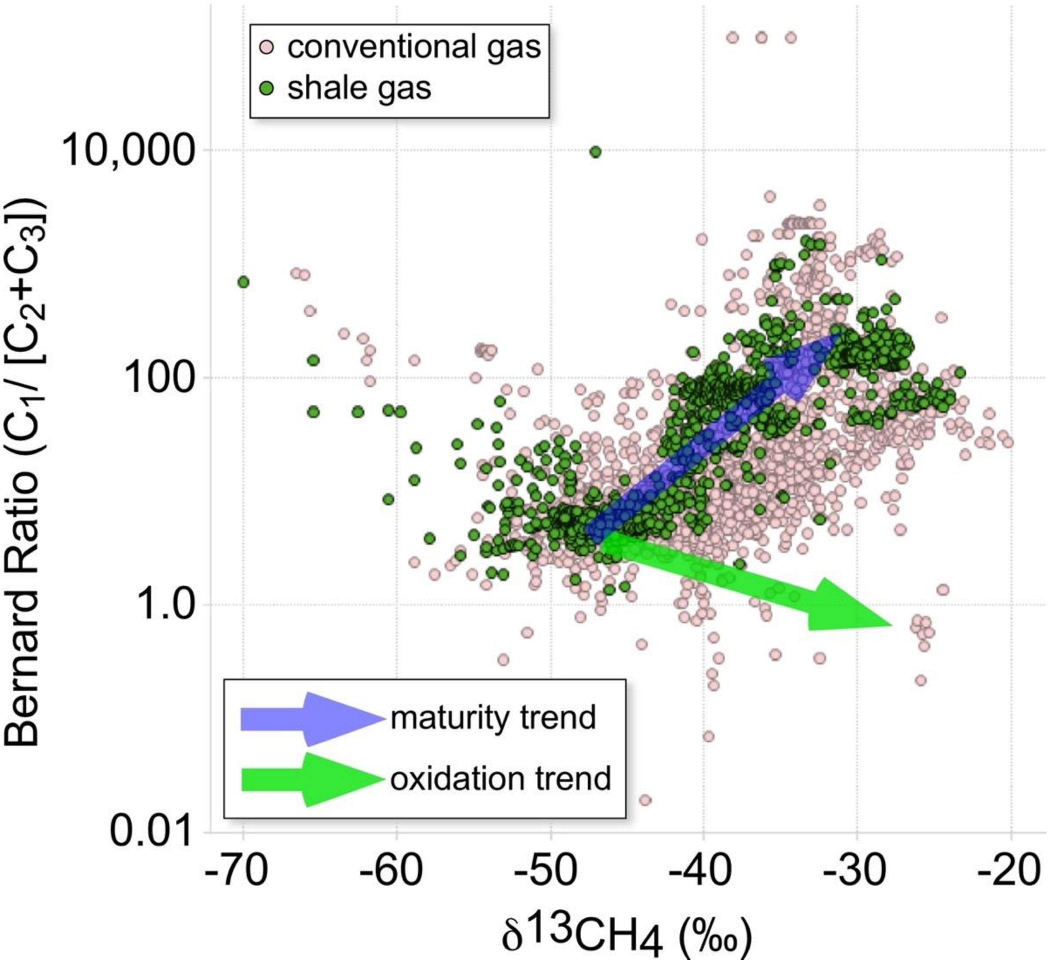


Figure 3. Bernard plot of gas wetness versus $\delta^{13}CH_4$ of CG and SG from Milkov et al. (2020) showing maturation trend and methane oxidation trend.

Furthermore, the hypothesis put forward in Howarth (2019) calling for extensive oxidation of methane in conventional natural gas, is inconsistent with the extensive observations of $\delta^{13}CH_4$ compared with $\delta^{13}C_2H_6$ and $\delta^{13}C_3H_8$ for thermogenic gases. The isotope offsets between $\delta^{13}CH_4$, $\delta^{13}C_2H_6$ and $\delta^{13}C_3H_8$ have been well established for thermogenic hydrocarbons (e.g., Stahl, 1973, James 1983, Faber, 1987, Jenden et al., 1988, Berner and Faber, 1988, 1996, Clayton, 1991, Rooney et al., 1995). These are largely determined by source type and thermal maturity, including isotope reversals at high maturity (e.g., Burruss and Laughrey, 2010, Zumberge et al., 2012, Tilley and Muehlenbachs, 2013, Cao et al., 2015, Han et al., 2018) and to a lesser extent by secondary effects, such as mixing and TSR (e.g., Krouse et al., 1988, Pan et al., 2006, Cai et al., 2010).

The AR1 (2020) never addresses the data in Table 1 that is contrary to the migration hypothesis. Yes, “proper” refers to gases produced from shales and not gases that have migrated away from the generating shale. The AR1 (2020) never discusses this, which is described in the text (Lines 76-85). The mean of 1,502 proper Marcellus gases is -32.4 ± 3.8‰ and the stratigraphically highest reservoir collecting migrated gases is -42.1 ± 6.29‰ in the Castkill/Lochaven reservoirs, which are contrary to the oxidation migration hypothesis by Howarth (2019) that the migrated conventional gases should have isotopically heavier $\delta^{13}C_1$ values than the shale gases.

Lines 121-131: Some clarification is needed here with regards to using the data reported by Baldassare et al. (2014) as evidence that the migration oxidation hypothesis is not valid as mentioned in the previous paragraph. In brief, the data set presents $\delta^{13}CH_4$ data for gases in rock units above the Marcellus. The Castkill/Lochaven reservoirs are stratigraphically the most distant and have a mean of -42.1 ± 6.3‰. If this gas was entirely sourced from the Marcellus and migrated upward from it, then according to the migration hypothesis by Howarth (2019) it should have a carbon isotope ratio more ^{13}C-enriched than that measured for the Marcellus shale gas (i.e., -32.4 ± 3.8 ‰), which it does not. Although, this contradicts the migration hypothesis by Howarth (2019), i.e., that conventional gas should be more ^{13}C-enriched than shale gas, the observed isotope trend can be explained by microbial gas from ground water input in the shallower reservoirs. Baldassare et al. (2014) suggested that less thermally mature gas from the Marcellus could be migrating up into the higher stratigraphic units. Regardless of the cause, these caveats negate any evidence for the migration hypothesis proposed by Howarth (2019).

The repeated notion by AR1 (2020) that the Chinese shale gas $\delta^{13}CH_4$ values are not completely shale gas and may include some conventional gas is not justified and inappropriately excludes these data from the mean value for ^{13}C-enriched $\delta^{13}CH_4$ values of shale gas that have been used by Howarth (2019). Feng et al. (2017) clearly state that the gases are from shale gas production in the Longmaxi Formation in the Weiyuan and Changing districts of the Sichuan Basin. Irrespective of whether these are from vertical or horizontal wells, the gases are produced from shale and are unlikely to have experienced any significant migration. The statement by AR1 (2020) that there was no commercial shale gas production from the Longmaxi Fm at the writing of Howarth (2019) is not pertinent. However, in the meanwhile, the Longmaxi Fm is being produced and the $\delta^{13}CH_4$ values of the produced shale gases do not negate the observation that these high thermally mature shale gases are, as expected, ^{13}C-enriched, i.e., $\delta^{13}CH_4 = -29.2 \pm 1.2$ ‰) than the $\delta^{13}{}_{CH4}$ mean value of -46.9 ± 0.4 ‰ that Howarth (2019) uses in his mathematical constructs. Milkov et al. (2020) reports for 230 Longmaxi Fm shale gas samples a mean $\delta^{13}CH_4$ of -30.3 ‰. These heavier values are expected for the high thermal maturities of these shales (% vitrinite reflectance between 1.85 and 4.2%; Cao et al., 2016) and considerably heavier compared to the mean value of Howarth (2019; i.e., $\delta^{13}CH_4 = -46.9$‰ ± 0.4).

Lines 150-152: The conclusion Lewan (2019) reached concerning greater input of biogenic methane to the atmosphere than shale gas is a result of simply using the rationale and mathematical constructs of Howarth (2019) with a more representative data set for shale gas $\delta^{13}CH_4$. This is contrary to Howarth (2019) concluding shale gas is a major contributor of atmospheric methane based on an inappropriate and non-representative data set for shale gas $\delta^{13}CH_4$ values. These result in substantial differences that need to be noted in addition to the sensitivity of using only $\delta^{13}CH_4$ values alone, as discussed by Turner et al. (2019).

Lines 146-151: This comment is redundant from the AR1 (2020)'s early comment about the difference being small on a percentage basis. As responded above for Lines 150-152, these differences force a big change in the final analysis of sources of methane emissions. The AR1 (2020) also alludes to this in earlier comments. As previously stated, conclusions by Lewan (2019) are based on the same rationale and mathematical constructs as described by Howarth (2019) with the only difference being the data set used for shale gas $\delta^{13}CH_4$. Howarth (2019) data set as Lewan (2019) has explained in the original comment and this discussion appears to favor choosing isotopically light $\delta^{13}CH_4$ values for shale gas rather than isotopically heavier values more representative of shale gas.

According to the mathematical constructions based on the argument by Howarth (2019), as the shale gas $\delta^{13}CH_4$ mean becomes more negative the input of shale-gas methane emissions increases and as the shale gas $\delta^{13}CH_4$ mean becomes more positive its methane emissions from shale gas diminishes. This is shown in Figure 3 where the $\delta^{13}CH_4$ of shale gas is changed in the scheme by Howarth (2019) to show the resulting emissions from biogenic, conventional gas and shale gas using a mass balance for total methane emissions of 28.4 Tg/yr prescribed by Worden et al. (2017; Howarth, 2019, equation 2). At the crossover $\delta^{13}CH_4$ value of -47.9 ‰ the shale gas emissions will start exceeding the microbial methane emissions. Figure 4 shows that the mean -46.9 ‰ value of Howarth (2019) is close to this point but highly exaggerated compared to Lewan (2019) and those shale gas means of Milkov et al. (2020). The two values from Milkov are interesting in that one value of mean $\delta^{13}CH_4$ value is just an arithmetic mean of -41.3 ± 0.2‰ for 1,619 samples and the other mean of -41.8‰ is a mean weighted by the amount of emissions measured in 2015 from main USA shale plays. The means of Milkov et al. (2020) and Lewan (2019) show the inappropriateness of Howarth (2019) data set for shale gas.

Howarth (2019) provides rational and mathematical constructs to evaluate source of methane emissions (Figure 4). This contribution would be more valuable if the data set were more representative of true shale gas production. The input $\delta^{13}CH_4$ values used by Howarth (2019) are not representative or appropriate for concluding that shale gas is the major driver for increasing atmospheric methane emissions. Indeed, we conclude that there is overwhelming evidence suggesting the main input of Howarth (2019) must be revised.

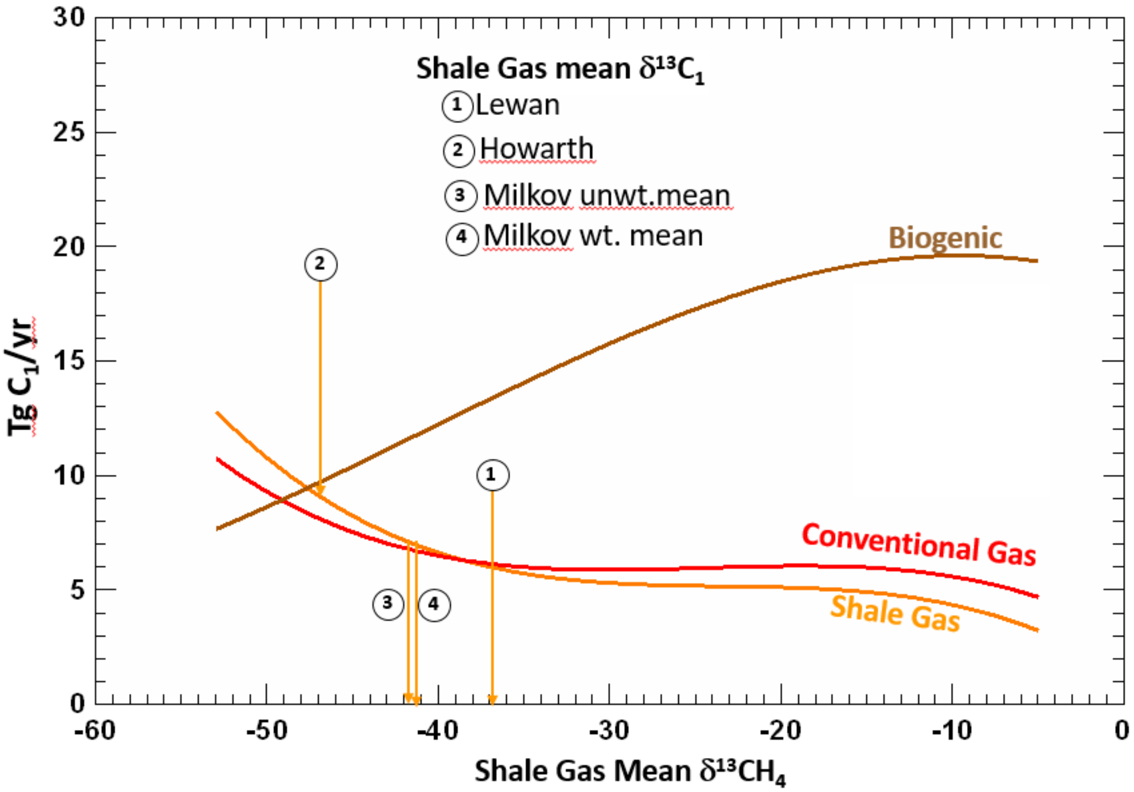


Figure 4. Plot of the sources of methane emissions from Biogenic, conventional and shale gas sources as a result of mean δ^{13}CH$_4$ values used for shale gas according to the rationale and mathematical constructs of Howarth (2019).

Just because Howarth may make a statement about the effects of thermal maturation or the broad range of δ^{13}CH$_4$ values does not mean he has incorporated these geochemistry concepts in his "Ideas and perspectives: is shale gas a major driver in global atmospheric methane". The bias in Howarth (2019) ^{13}C-depleted δ^{13}CH$_4$ values for shale gases is demonstrably incorrect and renders the conclusions on global methane emissions from major sources invalid. Future methane-emission studies are needed, and as noted by Lewan and previously by Turner et al. (2019) they should not be based solely on δ^{13}CH$_4$ to distinguish methane shale-gas emissions from various thermogenic sources of natural gases. As an example, stable hydrogen isotopes of methane (δD) are influenced by the δD of pore waters associated with organic matter during thermogenic generation of natural gas (Dias et al., 2014), and may provide a more definitive attribute in identifying related and different types of thermogenic methane sources.

References

Alperin, M.J., Reeburgh, W.S., and Whiticar, M.J.: Carbon and hydrogen isotope fractionation resulting from anaerobic methane oxidation. Global biogeochemical Cycles 2(3) 279-288, 1988.

Anonymous Referee #1: Interactive Comment on: “Comment on “Ideas and Perspectives: is shale gas a major driver of recent increase in global atmospheric methane?” by Robert W. Howarth (2019)” By Michael D. Lewan. Biogeosciences Discussion, https://doi.org/10.5194/bg-2019-419-RC1, 2020.

Baldassare, F. J., McCaffrey, M. A., and Harper, J.A.: A geochemical context for stray gas investigations in northern Appalachian Basin: Implications of analyses of natural gases from Neogene-through Devonian age strata, AAPG Bull. 98, 341-372, https//doi.org/10.1306/06111312178, 2014.

Berkman, T., Ellis, L., Grass, D.: Integration of mud gas isotope data with field appraisal at Horn Mountain Field, deepwater Gulf of Mexico. Successful Application of Non-Seismic Techniques to Exploration. AAPG Annual Mtg., March 13–16, Houston, Texas, Printed Abstracts (Supplement). AAPG Bulletin, vol. 86, 2002.

Bernard, B.B.: Light hydrocarbons in marine sediments. PhD thesis, Texas A&M University, College Station, Texas, pp. 144, 1978.

Berner, U. and Faber, E.: Maturity related mixing model for methane, ethane and propane, based on carbon isotopes. In Organic Geochemistry In Petroleum Exploration (pp. 67-72). Pergamon, 1988.

Berner, U. and Faber, E.: Empirical carbon isotope/maturity relationships for gases from algal kerogens and terrigenous organic matter, based on dry, open-system pyrolysis. *Organic Geochemistry, 24*(10-11), pp.947-955, 1996.

Boetius, A., Ravenschlag, K., Schubert, C.J., Rickert, D., Widdel, F., Giesecke, A., Amann, R., Jørgensen, B.B., Witte, U., Pfannkuche, O.: A marine microbial consortium apparently mediating anaerobic oxidation of methane. Nature 407, 623–626, 2000.

Botner, E. C., Townsend-Small, A., Nash, D. B., Xu, X., Schimmelmann, A., and Miller, J. H.: Monitoring concentrations and isotopic composition of methane in groundwater in the Utica Shale hydraulic fracturing region of Ohio, Envirin. Monit. Assess., 190, 322-337, https://doi.org/10.1007/s10661-018-6696-1, 2018.

Burgers, W.F.J. & Northrop, P.S. & Kheshgi, H.S. & Valencia, Jair.: Worldwide development potential for sour gas. Energy Procedia. 4. 2178-2184. 10.1016/j.egypro.2011.02.104, 2011.

Burruss, R. C. and Laughrey, C. D.: Carbon and hydrogen isotopic reversals in deep basin gas: evidence for limits to the stability of hydrocarbons, Org. Geochem., 41, 1285-1296, https://doi.org/10.1016/j.orggeochem.2010.09.008, 2010.

Cai, C., Li, K., Zhu, Y., Xiang, L., Jiang, L., Cai, X., & Cai, L.: TSR origin of sulfur in Permian and Triassic reservoir bitumen, East Sichuan Basin, China. Organic Geochemistry, 41(9), 871-878, 2010.

Cao, C., Tang, Q., Zhang, M., Zonggang, L.V.: Carbon Isotope Reversals of Changning-Weiyuan Region Shale Gas Sichuan Basin, Acta Geologica Sinica, 89 supp., http://www.geojournals.cn/dzxben/ch/index.aspx, 2015.

Chung, H. M., & Sackett, W. M.: Use of stable carbon isotope compositions of pyrolytically derived methane as maturity indices for carbonaceous materials. *Geochimica et Cosmochimica Acta*, *43*(12), 1979-1988. doi:10.1016/0016-7037(79)90010-3, 1979.

Claypool G.E., Kaplan I.R.: The Origin and Distribution of Methane in Marine Sediments. In: Kaplan I.R. (eds) Natural Gases in Marine Sediments. Marine Science, vol 3. Springer, Boston, pp 99-139, 1974.

Clayton, C.: Carbon isotope fractionation during natural gas generation from kerogen. Marine and petroleum geology, 8(2), 232-240, 1991.

Coleman D. D., Risatti J. B. and Schoell M.: Fractionation of carbon and hydrogen isotopes by methane oxidizing bacteria. Geochim. Cosmochim. Acta 45, 1033-1037, 1981.

Cramer B, Krooss BM, Littke R.: Modelling isotope fractionation during primary cracking of natural gas: a reaction kinetic approach. Chemical Geology;149:235-250, 1998.

Curtis, J.B.: Fractured shale-gas systems, AAPG Bulletin, 86, 1921-1938, 2002.

Dawson, D. and Murray, A.: Natural gas geochemistry: recent developments, applications, and technologies: AAPG Search and Discovery Article #90134, 1-3, 2011.

Ellis, L., Brown, A., Schoell, M., and Haught, M.: “Mudgas isotope logging while drilling: A new field technique for exploration and production”, 19th International Meeting on Org. Geochem., 6-10 September 1999, Istanbul, Turkey, Abstracts Part I, p. 67-68, 1999.

Ellis, L., Brown, A., Schoell, M., and Uchytil, S.: “Mud gas isotope logging (MGIL) assists in oil and gas drilling operations” Oil & Gas Journal, v. 101, Issue 21, 2003.

Faber, E.: Zur Isotopengeochemie gasformiger Kohlenwasserstoffe. Erdoel, Erdgas, Kohle, 103: 210,1987

Feisthauer, S., Vogt, C., Modrzynski, J., Szlenkier, M., Krüger, M., Siegert, M., and Richnow, H.H.: Different types of methane monooxygenases produce similar carbon and hydrogen isotope fractionation patterns during methane oxidation. Geochimica et Cosmochimica Acta, 75(5), 1173-1184, 2011.

Feng, Z., Huang, S., Wu, W., Xie, C., Peng, W., and Cai, Y.: Longmaxi shale gas geochemistry in Changning and Fuling gas fields, the Sichuan Basin, EnergyExploration & Exploitation, 35, 259-278, 2017.

Gaswirth, S. B. and Marra, K. R.: U.S. Geological Survey 2013 assessment of undiscovered resources in the Bakken and Three Forks Formations of the U.S. Williston Basin Province: AAPG Bulletin, 99, 639-660, 2015.

Golding, S. D., Boreham, C. J., and Esterle, J. S.: Stable isotope geochemistry of coal bed and shale gas and related production waters: A review, Int. J. Coal Geolog., 120, 24–40, https://doi.org/10.1016/j.coal.2013.09.001, 2013.

Gong, D., Huang, S., Wu, W., Yu, C., Fang, C., & Liu, D.: Characteristics of gas compositions in giant gas fields of china. *Energy Exploration & Exploitation*, *32*(4), 635-656. doi:10.1260/0144-5987.32.4.635, 2014.

Grant, N.J., and Whiticar, M.J., Stable carbon isotopic evidence for methane oxidation in plumes above Hydrate ridge, Cascadia Oregon, Margin, Global Biochemical Cycles, 16, 71-84, 2002.

Han, W., Ma, W., Tao, S., Huang, S., Hou, L., & Yao, J.: Carbon isotope reversal and its relationship with natural gas origins in the jingbian gas field, ordos basin, china. International Journal of Coal Geology, 196, 260-273. doi:10.1016/j.coal.2018.06.024, 2018.

Hanson, R.S., and Hanson, T.E.:.Methanotrophic bacteria. Microbiological Reviews, 60(2), 439–471, 1996.

Harrison, A.G., Thode, H.G.: The kinetic isotope effect in the chemical reduction of sulfate. Trans. Faraday Soc. 53, 1–4, 1957.

Hao, F. and Zou, H.: Cause of shale gas geochemical anomalies and mechanisms for gas enrichment and depletion in high-maturity shales, Mar. Petrol. Geol., 44, 1-12, https://doi.org/10.1016/j.marpetgeo.2013.03.005, 2013.

Hinrichs, K.-U.; Boetius, A.: The Anaerobic Oxdiation of Methane: New Insights in Microbial Ecology and Biogeochemistry. In Ocean Margin Systems; Wefer, G., Billett, D., Hebbeln, D., Jorgensen, B.B., Schlüter, M., Weering, T.V., Eds.; Springer: Berlin, pp. 457–477, 2002.

Hoehler, T.M., M.J. Alperin, D.B. Albert, and C.S. Martens.: Field and laboratory studies of methane oxidation in an anoxic marine sediment: Evidence for a methane-sulfate reducer consortium. Global Biogeochem. Cycles 8:451–463, 1994.

Howarth, R. W.: Ideas and perspectives: is shale gas a major driver of recent increases in global atmospheric methane?, Biogeosciences, 16, 3033-3046, 2019.

Jackson, R.B., Vengosh, A., Darrah, T.H., Warner, N.R., Down, A., Poreda, R.J., Osborn, S.G., Zhao, K., Karr, J.D.: Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction, PNAS, www.pnas.org/cgi/doi/10.1073/pnas.1221635110, 2013.

James, A. T.: Correlation of natural gas by use of carbon isotopic distribution between hydrocarbon components Am. Assoc. Petrol GeoL Bull. 67, 1176-1191, 1983.

Jarvie, D.M.: Shale Resources systems for oil and gas: Part 1-Shale gas resource Systems, in Shale reservoirs-Giant resources for the 21st Century (ed. J.A. Beyer): AAPG Memoir 97, 69-87, 2012.

Jenden, P. D., Newell, K. D., Kaplan, I. R., & Watney, W. L.: Composition and stable-isotope geochemistry of natural gases from Kansas, midcontinent, U.S.A. *Chemical Geology, 71*(1), 117-147. doi:10.1016/0009-2541(88)90110-6, 1988.

Jenden, P. D., Hilton, D. R., Kaplan, I. R., and Craig, H.: Abiogenic hydrocarbons and mantle helium in oil and gas fields: in D. G. Howell, ed., The Future of Energy Gases, U.S. Geological Survey Professional Paper 1570, 31-56, 1993.

King, G.M..: Ecological aspects of methane oxidation, a key determinant of global methane dynamics. Adv. Microb. Ecol. 12, 431–468, 1992.

Kinnaman, F. S., Valentine, D. L., & Tyler, S. C.: Carbon and hydrogen isotope fractionation associated with the aerobic microbial oxidation of methane, ethane, propane and butane. Geochimica Et Cosmochimica Acta, 71(2), 271-283. doi:10.1016/j.gca.2006.09.007, 2007.

Krouse, H.R., Viau, C.A., Eliuk, L.S., Ueda, A., Halas, S.: Chemical and isotopic evidence of thermal-chemical sulphate reduction by light hydrocarbon gases in deep carbonate reservoirs, Nature 333, 415–419, 1988.

Kulongoski, J.T., McMahon, P.B., Land, M., Wright, M.T., Johnson, T.A., and Landon, M.K.: Origin of methane and sources of high concentrations in Los Angeles groundwater: Journal of Geophysical Research: Biogeosciences, 123, 818-831, 2018.

Larter S., Hung H., Adams J., Bennett, B., Jokanola, O., Jones m., Head I., Riediger C., Fowler M.: The controls on the composition of biodegraded oils in the deep subsurface: Part II- Geological controls on subsurface biodegradation fluxes and constraints on reservoir-fluid property prediction. American Association of petroleum Geology Bulletin, 90, 921-938, 2006.

Lan, X., Tans, P., Sweeney, C., Andrews, A., Dlugokencky, E., Schwietzke, S., Kofler, J., McKain, K., Thoning, K., Crotwell, M., Montzka, S., Miller, B. R., and Biraud, S. C.: Long-term measurements show little evidence for large increases in total U.S. methane emissions over the past decade, Geophysical Research Letters, 49, 4991-4999, https://doi.org/10.1029/2018GL081731, 2019.

Lebedew W. C., Owsjannikow W. M., Mogilewskij G. A. and Bogdanow W. M.: Fraktionierung der Kohlenstoffisotope durch mikrobiologische Prozesse in der biochemischen Zone. Angew. Geol. 12, 621-624, 1969.

Lewan, M.D.: Comments on “Ideas and perspectives:is shale gas a major driver of recent increase in global atmospheric methane?” Biogeosciences, 2020.

Lindstrom, M.E.: Aerobic methylotrophic prokaryotes. In Dworkin, M. (ed.), The Prokaryotes. New York: Springer, Vol. 2, 618–634, 2006.

Machel, H. G., Krouse, H. R., & Sassen, R.: Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. *Applied geochemistry*, *10*(4), 373-389, 1995.

Machel, H.G.: Bacterial and thermochemical sulfate reduction in diagenetic settings — old and new insights. Sedimentary Geology, 140(1), 143-175, 2001.

Mariotti, A., Germon, J.C., Hubert, P. *et al.* Experimental determination of nitrogen kinetic isotope fractionation: Some principles; illustration for the denitrification and nitrification processes. Plant Soil 62, 413–430,1981.

Martens, C. S., and Berner, R.A.: Methane production in the interstitial waters of sulfate-depleted marine sediments. Science, 185(4157), 1167-1169, 1974.

Martini, A. M., Walter, L. M., Budai, J. M., Ku, T. C. W., Kaiser, C. J., and Schoell, M.: Genetic and temporal relations between formation waters and biogenic methane: Upper Devonian Antrim Shale, Michigan Basin, USA, Geochim. Cosmochim. Ac., 62, 1699-1720, 1998.

McIntosh, J. C., Walter, L. M., and Martini, A. M.: Pleistocene recharge to mid-continent basins: effects on salinity structureandmicrobial gas generation, Geochim.Cosmochim.Ac.,66,1681-1700, https://doi.org/10.1016/S0016-7037(01)00885-7, 2002.

McKinney, D. E., Flannery, M., Elshahawi, H., Stankiewicz, A., Clarke, E., Breviere, J., & Sharma, S.: Advanced Mud Gas Logging in Combination with Wireline Formation Testing and Geochemical Fingerprinting for an Improved Understanding of Reservoir Architecture. Society of Petroleum Engineers. doi:10.2118/109861-MS, 2007.

Milkov, A.V., Schwietzke, S., Allen, G., Sherwood, O.A., and Etiope, G.: Using global isotopic data to constrain the role of shale gas production in recent increases in atmospheric methane: Scientific Reports, Natureresearch, Https://doi.org/10.1038/s41598-020-61035, 2020.

Muehlenbachs, K., and Arismendi, G.G.: The Isotopic Composition of Fugitive Greenhouse Gases From Energy Wells of the Western Canada Sedimentary Basin, AGUFM, B23D-07, 2019.

Nisbet, E.G., Dlugokencky, E.J., Manning, M.R., Lowry, D., Fisher, R.E., France, J.L., Michel, S.E., Miller, J.B., White, J.W.C., Vaughn, B. and Bousquet, P.: Rising atmospheric methane: 2007-2014 growth and isotopic shift. Glob Biogeochem Cy 30:1356–1370, 2016.

Orphan, V.J., Hinrichs, K.-U., Ussler, W., III, Paull, C.K., Taylor, L.T., Sylva, S.P., et al.: Comparative analysis of methane-oxidizing archaea and sulfate-reducing bacteria in anoxic marine sediments. Appl Environ Microbiol 67: 1922–1934, 2001.

Orr, W.L.: Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation—study of Big Horn Basin Paleozoic oils. AAPG Bull. 58, 2295–2318, 1974.

Orr, W.L.: Geologic and geochemical controls on the distribution of hydrogen sulfide in natural gas. In: Campos, R., Goni, J. (Eds.), Advances in Organic Geochemistry, 1975, Madrid, Spain. Pergamon Press, Oxford, pp. 571–

597, 1977.

Osborn, S. G. and McIntosh, J. C.: Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic rich shales and reservoir sandstones, northern Appalachian Basin, Appl. Geochem,. 25, 456-471, https://doi.org/10.1016/j.apgeochem.2010.01.001, 2010.

Pan, C., Yu, L., Liu, J., & Fu, J.: Chemical and carbon isotopic fractionations of gaseous hydrocarbons during abiogenic oxidation. Earth and Planetary Science Letters, 246(1), 70-89. doi:10.1016/j.epsl.2006.04.013, 2006.

Penger, J., Conrad, R., and Blaser, M.: Stable carbon isotope fractionation by methylotrophic methanogenic archaea. Applied and Environmental Microbiology, 78(21), 7596-7602, 2012.

Rasigraf, O., Vogt, C., Richnow, H. H., Jetten, M. S., & Ettwig, K. F.: Carbon and hydrogen isotope fractionation during nitrite-dependent anaerobic methane oxidation by Methylomirabilis oxyfera. Geochimica et Cosmochimica Acta, 89, 256-264, 2012.

Reeburgh, W.S.: Methane consumption in Cariaco trench waters and sediments. Earth Plan Res Lett 28:337–344, 1976.

Riley,R.A., Mapping source rock and thermal maturity of the Devonian shale interval in eastern Ohio: Ohio Department of natural Resources, Division of Geological Survey Open-File Report 2016-2, 22p., 2016.

Rodriguez, N. D. and Philp, R. P.: Geochemical characterization of gases from the Mississippian Barnett shale, Fort Worth Basin, Texas, AAPG Bull., 94, 1641-1656, https://doi.org/10.1306/04061009119, 2010.

Rooney, M. A., Claypool, G. E., & Moses Chung, H.: Modeling thermogenic gas generation using carbon isotope ratios of natural gas hydrocarbons. *Chemical Geology, 126*(3-4), 219-232. doi:10.1016/0009-2541(95)00119-0, 1995.

Rooze, J., Egger, M., Tsandev, I., and Slomp,C. P.: Iron-dependent anaerobic oxidation of methane in coastal surface sediments: Potential controls and impacts, Limnol. Oceanogr., 61, S267-S282, https://doi.org/10.1002/lino.10275, 2016.

Stahl, W.: Carbon isotope ratios of German natural gases in comparison with isotopic data of gaseous hydrocarbons from other parts of the World. In: Advances in Organic Geochemistry, 1973 (Eds. B. Tissot and F. Bienner) Editions Technip, Paris, pp. 453-462, 1973.

Stahl, W. J., & Carey, B. D.: Source-rock identification by isotope analyses of natural gases from fields in the val verde and delaware basins, west texas. *Chemical Geology, 16*(4), 257-267. doi:10.1016/0009-2541(75)90065-0, 1975.

Schaefer, H., Mikaloff-Fletcher, S. E., Veidt, C., Lassy, K.R., Brailsford, G.W., Bromley, T.M., Dlubokencky, E.J., Michel, S.E., Miller, J.B., Levin, I., Lowe, D.C., Martin, R.J., Vaugn, B.H., and White, J.W.C.: A 21st century shift from fossil-fuel to biogenic methane emissions indicated by $^{13}CH_4$, Science, 352, 80-84, https://doi.org/10.1126/science.aad2705, 2016.

Schoell, M.: The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochimica et Cosmochimica Acta*, *44*(5), 649-661, 1980.

Schoell, M. and LeFever, J.A., Carbon and hydrogen isotope systematics in gases from horizontal Bakken Shale WELLS: aapg Search and Duscovery Article #110149, 2011.

Schoell, M., Lefever, J.A., and Dow, W.: Use of maturity related changes in gas isotopes in production and exploration of Bakken shale plays, AAPG Search and Discovery Article no. 90122©2011, AAPG Hedberg Conference, 5-10 December 2010, Austin, Texas, available at: http://www.searchanddiscovery.com/abstracts/pdf/2011/hedberg-beijing/abstract/ndx_schoell.pdf (last access: 25 September 2019), 2011.

Schwietzke, S., Sherwood, O.A., Bruhwiler, L.M.P., Miller, J.B., Etiope, G., Dlubokencky, E.J., Michel, S.E., Arling, V.A., Vaugn, B.H., White, J.W.C., and Tans, P.P.: Upward revision of global fossil fuel methane emissions based on isotope database, Nature, 538, 88-91, 2016.

Sherwood, O.A., Schwietzke, S., Arling, V.A., and Etiope, G: Global Inventory of Gas Geochemistry Data from Fossil Fuel, Microbial and Burning Sources, version 2017, Earth Syst. Sci. Data, 9, 63-656, https://10.5194/essd-9-639-2017, 2017.

Stankiewicz, B.A., McKinney, D., Breviere, J., Lessi, J., and Jaulneau, P., "Advanced mud logging technology – New Horizons in Petroleum Geochemistry", Abstract O85, 23rd International Meeting on Org. Geochem., 9-14 September 2007, Torquay, United Kingdom, 2007.

Tang Y., Perry J.K., Jenden P.D. and Schoell, M.: Mathematical modeling of stable carbon isotope ratios in natural gases. Geochim. Cosmochim. Acta 64, 2673–2687, 2000.

Thode, H.G., Monster, J., Dunford, H.B.,: Sulfur-isotope abundance in petroleum and associated materials. AAPG Bull. 42, 2619–2641, 1958.

Tilley, B., & Muehlenbachs, K.: Isotope reversals and universal stages and trends of gas maturation in sealed, self-contained petroleum systems. Chemical Geology, 339, 194-204. doi:10.1016/j.chemgeo.2012.08.002, 2013.

Townsend-Small, A., Marrero. J.E., Lyon, D. R., Simpson, I.J., Meinhardi, S., and Blake, D.R.: Integrating source apportionment tracers into a bottom up inventory of methane emissions in the Barnett Shale hydraulic fracturing region: Environmental Science & Technology, 49, 8175-8182, 2015.

Turner, A.J., Frankenberg, C., Kort, E.A.: Interpreting contemporary trends in atmospheric methane: PNAS 116, 2805-2813., 2016, Ambiguity in the causes for Decadal trends in atmospheric methane and hydroxyl, 2016.

Vigneron, A., Bishop, A., Alsop, E.B., Hull, K., Rhodes, I., Hendricks, R., head, I.M., and Tsesmetzis, N.: Microbial and isotopic evidence for methane cycling in hydrocarbon-containing groundwater from Pennsylvania Region: Frontiers in Microbiology, 8, article 593, 1-12, 2017.

Weissenburger, K.S. and Borbas, T.: Fluid properties, phase and compartmentalization: Magnolia Field case study, deepwater Gulf of Mexico: in, J.M. Cubitt, W.A. England, and S. Larter (eds.), Understanding Petroleum Reservoirs: Towards an Integrated Reservoir and Geochemical Approach, Geological Society, London, Special Publication 237, 231-255, 2004.

Whelan, J.K., Oremland, R., Tarata, M., Smith, R., Howarth, R., and Lee, C.: Evidence for sulfate reducing and methane producing microorganisms in sediments from sites 618,6116, and 622, Reports of the Deep-Sea Drilling Project, 47,767-775, https://doi.org/10.2973/dsdp.proc.96.147.1986, 1986.

Whiticar, M.J., and Faber, E.: Methane oxidation in sediment and water column environments—isotope evidence. Organic geochemistry, 10(4-6), 759-768, 1986.

Whiticar, M.J.: Correlation of natural gases with their sources, *in* L.B. Magoon and W. G. Dow, eds., The petroleum system-from source to trap: AAPG Memoir 60, 261-283, 1994.

Whiticar, M.J.: Carbon and hydrogen isotope systematic of microbial formation and oxidation of methane. Chem. Geol. 161, 291–314, 1999.

Worden, R.H., Smalley, P.C., Oxtoby, N.H.: Gas souring by thermochemical sulfate reduction at 140 °C. AAPG Bull. 79, 854–863, 1995.

Worden, J.R., Bloom, A.A., Pandey, S., Jiang, Z., Worden, H., Walter, M., Houweiling, S., and Rockman, T.: Reduced biomass burning emissions reconcile conflicting estimates of the post-2006 atmospheric methane budget, Nat. Commun., 8, 2227, 2017.

Zhang, T. and Krooss, B.M.: Experimental investigation on the carbon isotope fractionation of methane during gas migration by diffusion through sedimentary rocks at elevated temperature and pressure, Geochim. Cosmochim. Ac., 65, 2723-2742, 2001.

Zumberge, J., Ferworn, K., and Brown, S.: Isotopic reversal ('rollover') in shale gases produced from the Mississipian Barnett and Fayetteville formations: Marine and Petroleum Geology, 31, 43-52, https://doi.org/10.1016/j.marpetgeo.2011.06.009, 2012.

Zyakun A.M., Bondar V.A. and Namsarayev B.B.: Fraktsionirovaniye stabil'niioykh izotopov ugleroda metana pri yego mikrobiologicheskom okisleni (Fractionation of stable carbon isotopes in methane during microbiological oxidation. Geochem. Int. 16, 164-169, 1979.