Global Inventory of Natural Gas Molecular & Isotopic Compositions

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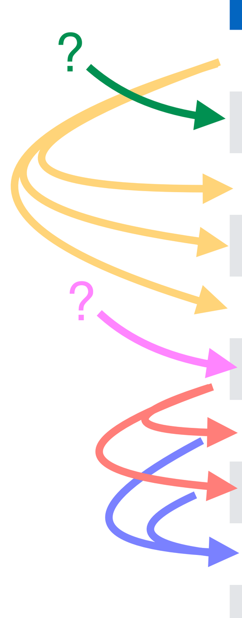
Introduction

Top-down models of the global atmospheric methane budget use isotopic and/or molecular data to constrain source-specific emissions. These models are sensitive to end-member signatures ($\delta^{13}C_{CH4}$, δD_{CH4}, ethane:methane ratios) for the three main source categories, microbial methanogenesis, biomass burning, and fossil fuels. However, the end-member values are poorly constrained and based on data of unknown or limited sample count, regional extent and global representation. For fossil fuels in particular, few modeling studies reference primary data, despite a vast literature in petroleum geology reporting on the isotopic and molecular composition of natural gas.

Table 1: Natural gas and coal $\delta^{13}C_{CH4}$ source signatures used in some top-down models of the global methane budget. Citation pathways indicated by arrows. Only one study (Whiticar 1989) is based on a large empirical dataset; however, the data were proprietary and therefore of unknown global or regional representation.



Reference	Natural Gas $\delta^{13}C_{CH4}$ (‰)	Coal $\delta^{13}C_{CH4}$ (‰)
Whiticar 1989	-44	-37
Gupta 1996	-38	-37
Quay 1999	-43 ± 7	-36 ± 7
Mikaloff 2004	-44	-37
Bousquet 2006	-44	-37
Lassey 2007	-40	-35
Neef 2010	-40	-35
Monteil 2011	-40	-35
Kirschke 2013	-55 to -25	N/A
Literature Average:	**-41.3 ± 2.7**	**-36.2 ± 0.1**

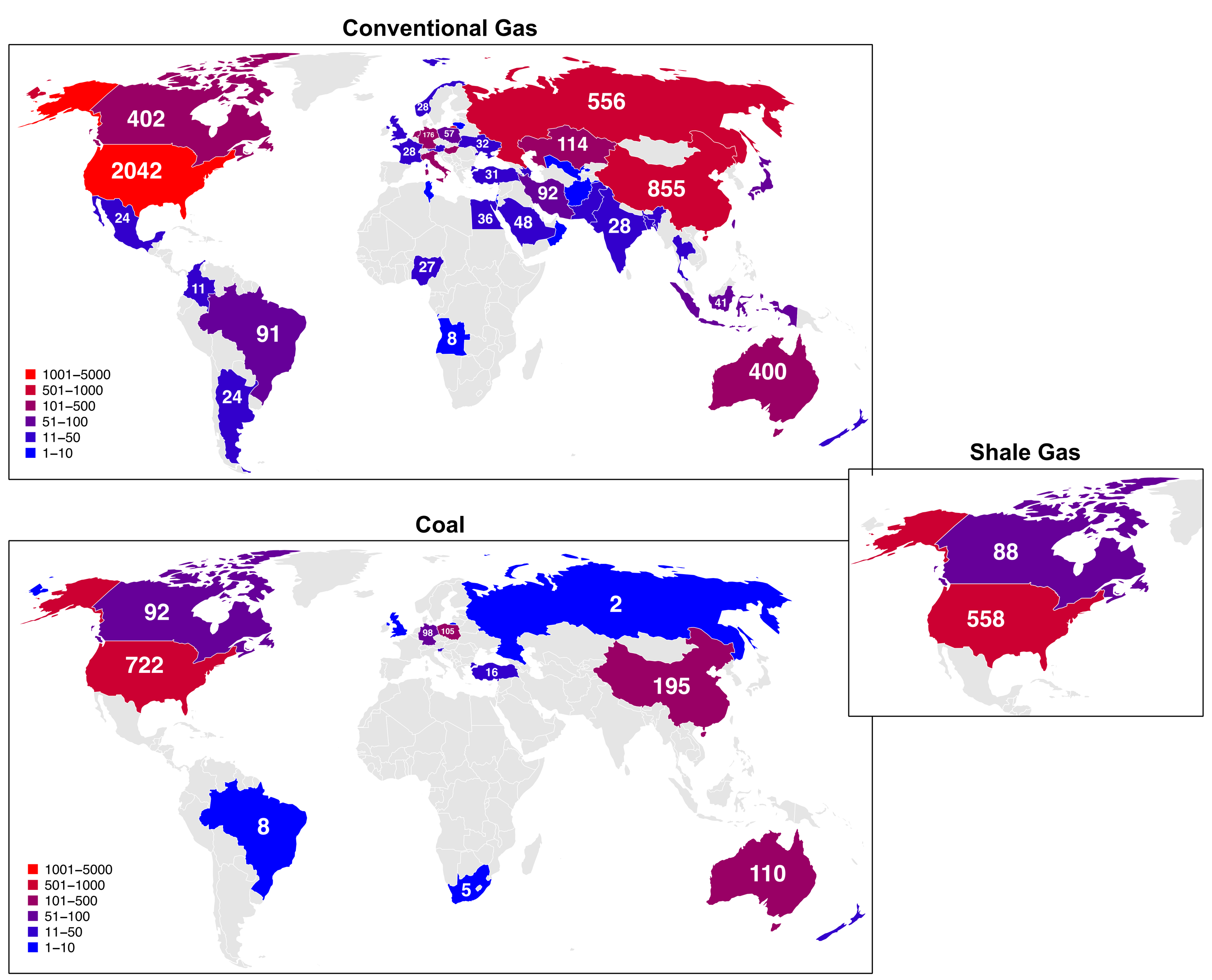


Fig. 1: Maps showing country-level sample counts for conventional natural gas, coal and shale gas data compiled from the literature and government reports. Shale gas data exist for USA and Canada only.

Database

We compiled a global inventory of natural gas molecular and isotopic measurements from the peer-reviewed literature and government reports (Fig. 1). Samples were categorized into conventional oil&gas, coal and shale gas. Recorded parameters include concentrations of C_1-C_6 alkanes and permanent gases and $\delta^{13}C$ and δD of C_1-C_6 alkanes.

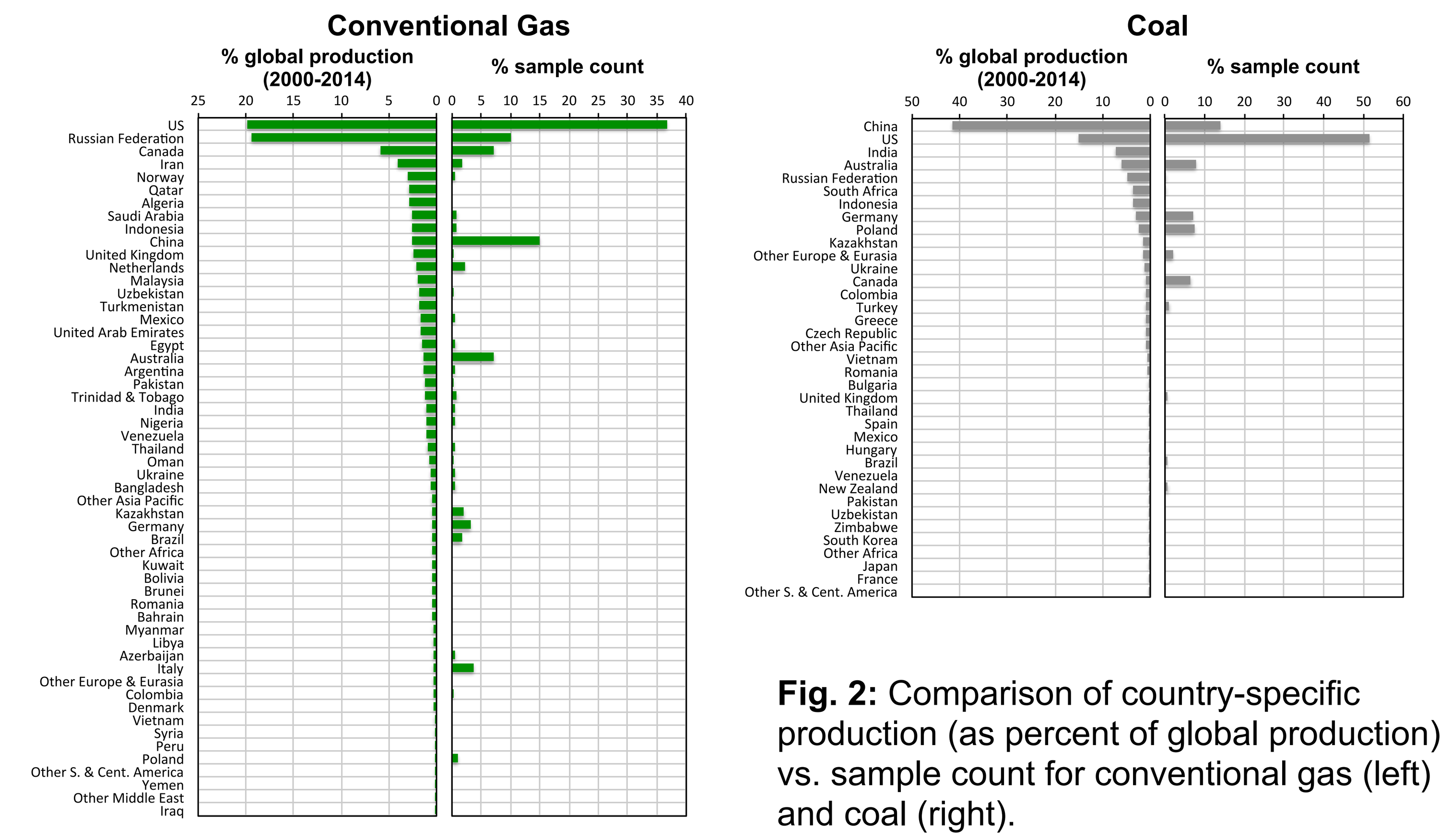


Fig. 2: Comparison of country-specific production (as percent of global production) vs. sample count for conventional gas (left) and coal (right).

Global Representation

The inventory contains data from 45 countries, 179 basins, >597 geological formations, and 8734 unique samples. On a country-level basis, the data represent 82.5% of world natural gas production and 80.2 % of world coal production over the period 2000-2014 (BP 2014). Note over-representation of some countries (e.g. USA, China, Australia) and under-representation of others (e.g. Norway, Qatar, Algeria, Saudi Arabia, Turkmenistan).

Caveats

- Focus was on publications having isotope data; much more gas concentration data exist in the literature/reports.
- No way to verify isotopic calibration/standardization (esp. Soviet era papers).

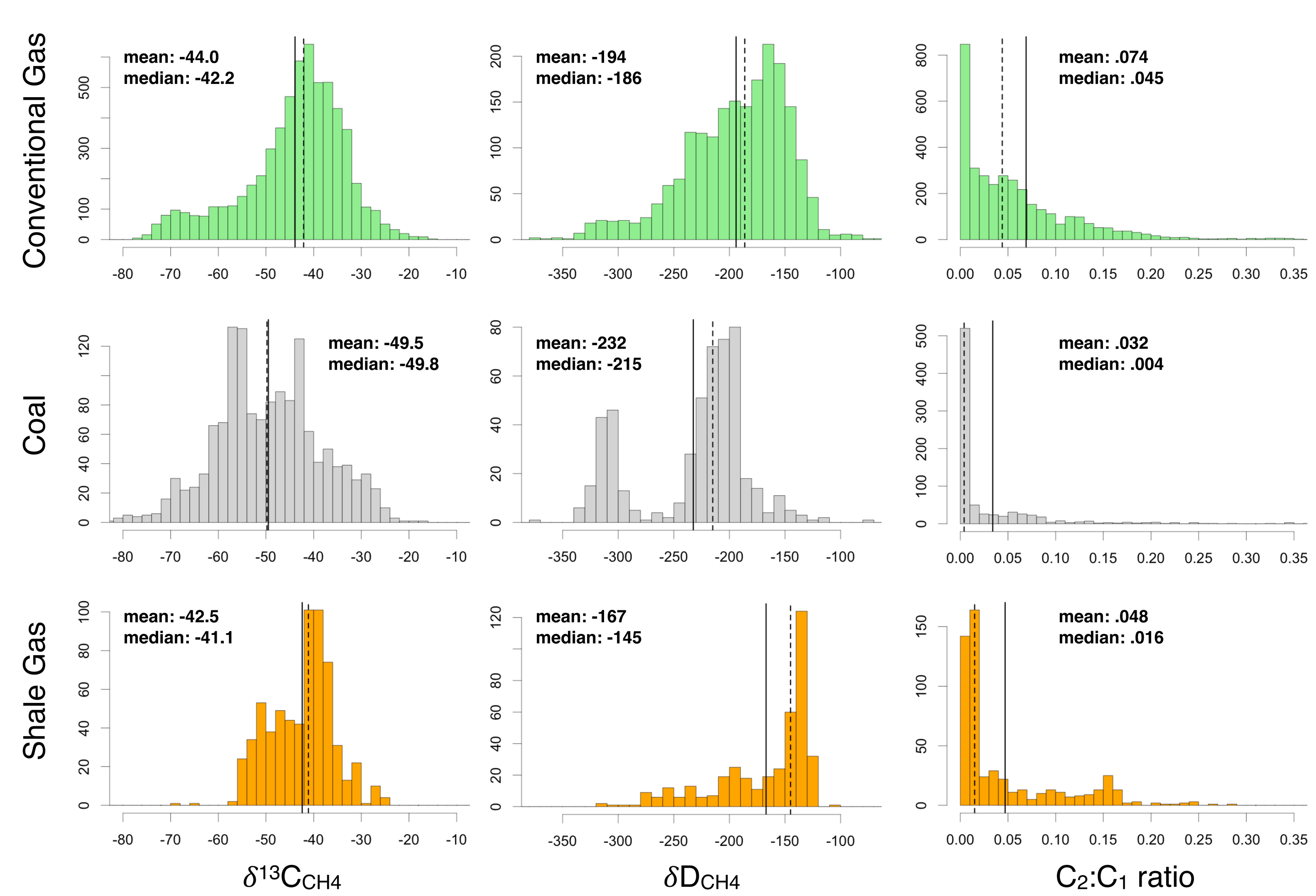


Fig. 3: Distributions of $\delta^{13}C_{CH4}$, δD_{CH4} and C_2:C_1 ratios for conventional gas, coal, and shale gas. Note skewed conventional gas distributions and bimodal coal distributions.

Implications for Top-Down Models

Data distributions are shown in Fig. 3. Note significantly lower mean and median $\delta^{13}C_{CH4}$ values for conventional gas and especially coal, than typically used in top-down models (Table 1). This is due to the importance of 1) primary and secondary microbial methanogenesis in approximately 20% of global oil and gas reservoirs (Rice & Claypool 1981; Milkov 2011) and in coal (Rice 1993) and 2) isotopically light signatures in low-maturity, oil-associated gas (Fig. 4). For example, giant Cenomanian gas pools of western Siberia, which account for 17% of global gas production, have mean $\delta^{13}C_{CH4}$ = -51 ‰. Revision of $\delta^{13}C_{CH4}$ end-member signatures has a significant effect on modeled fossil fuel contributions to the global methane budget (Schwietzke et al. submitted).

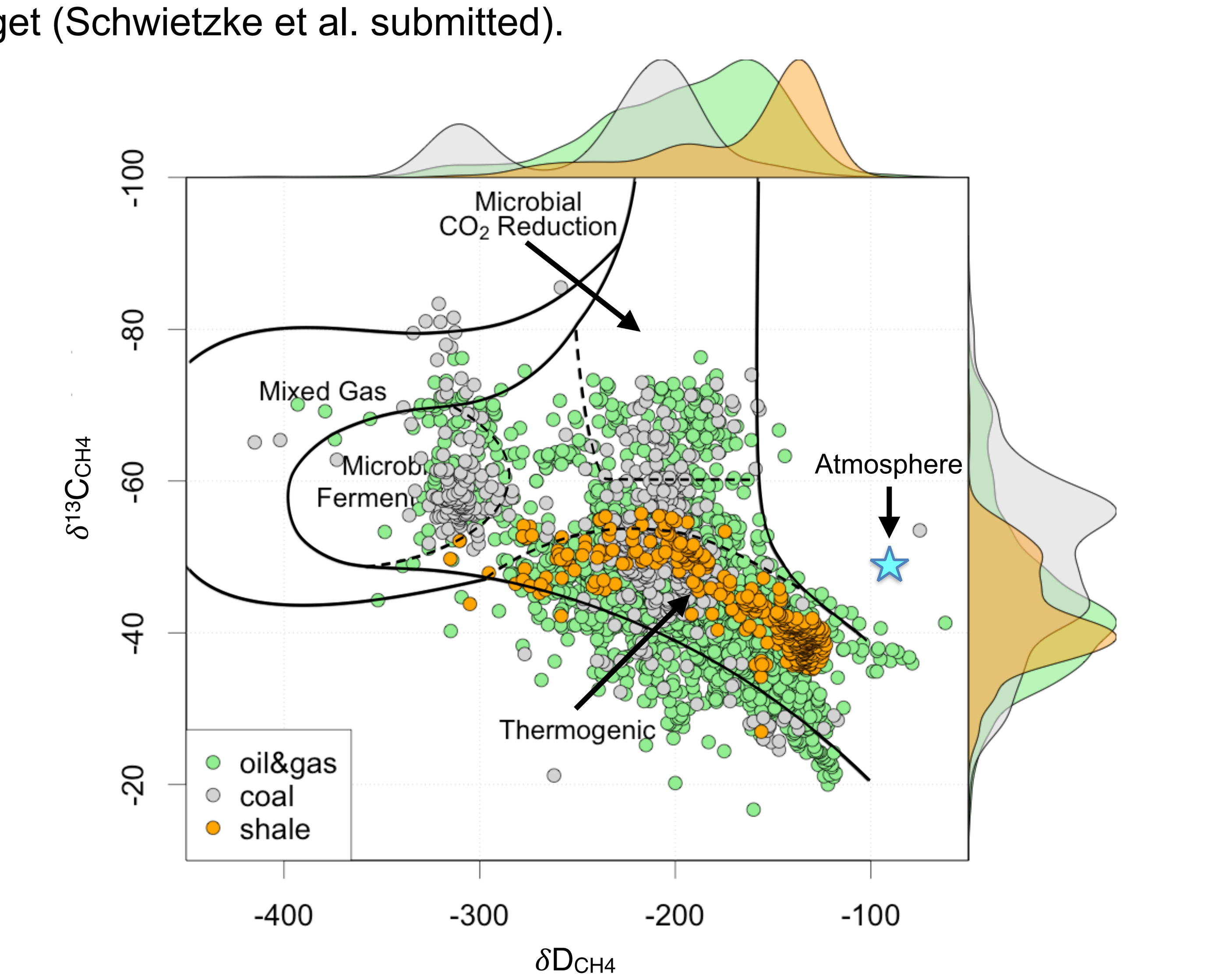


Fig. 4: Plot of $\delta^{13}C_{CH4}$ vs. δD_{CH4} for conventional gas, coal, and shale gas, with density distributions and genetic domains. Microbial methanogenesis (via fermentation and microbial CO_2 pathways) in conventional gas reservoirs and coal accounts for negatively-skewed $\delta^{13}C_{CH4}$ distributions.

Conclusions

- Most complete database of natural gas compositions ever compiled.
- Includes isotopic ($\delta^{13}C$ & δD) and molecular compositions.
- Data represent ~80% of global natural gas and coal production.
- At global level, $\delta^{13}C$ and δD values are skewed to lower values because of microbial methanogenesis and low thermal maturity oil-associated gases.
- Previous inversion studies may have underestimated the fossil fuel flux due to use of end-member values that were too high.
- Database will be published as a standalone manuscript and is available by download through:

  Sherwood, O., Schwietzke, S., Arling, V. & Etiope, G. Global Inventory of Fossil and Non-fossil Methane $\delta^{13}C$ Source Signature Measurements for Improved Atmospheric Modeling. (2016). doi:http://ezid.cdlib.org/id/doi:10.15138/G37P4D.

References

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