Does natural gas form in isotopic equilibrium?

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Natural gas is a key energy resource as the economy transitions to carbon-free energy systems, and understanding how it forms is important for predicting where it forms in economically important volumes. However, the origin of dry thermogenic natural gas is one of the most controversial topics in petroleum geochemistry, with several differing hypotheses, including kinetic processes (such as thermal cracking, phase partitioning during migration, demethylation of aromatic rings), and quasi-equilibrium processes (such as transition metal catalysis).

We have measured C and H isotopic compositions of light n-alkanes (C_1-C_5) and CO_2 as well as clumped methane compositions for 119 gases from 20 petroleum deposits around the world. This extended data base provides a far wider sampling than has been compiled before and allows us to use stricter tests of the kinetic and equilibrium hypotheses than have been previously considered.

Surprisingly we find that most of our measured C_2+ gases (ethane, propane, butane, and pentane) are in or closely approach isotopic equilibrium for carbon and hydrogen isotopes and are not consistent with the kinetic isotope effects associated with homolytic cleavage or beta scission (the dominant mechanism by which larger alkane precursors are cracked from larger n-alkanes). Interestingly, we also find that CO_2 and methane exhibit their own pattern of isotopic signatures, suggesting that they form a second, quasi-equilibrated population, separate from the C_2-C_5 compounds. These same patterns are also seen in a global compilation of 500+ natural gases. This conclusion implies that new approaches are needed for predicting the compositions of natural gases as functions of time, temperature and source substrate. We present a model for natural gas formation that explains these findings using cyclical networks of reactions that allow gases to evolve toward a metastable equilibrium. This model has implications for where economically feasible amounts of natural gas could be found. Additionally, an isotopically equilibrated state can serve as a reference frame for recognizing many secondary processes that may modify natural gases after their formation, such as biodegradation.