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Main Controls on Gas Chemistry in Shale Gas System: Evidence for Preservation of Methane in Core Samples from the Mudstones of the Eagle Ford Formation, TX

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Accurately determining oil-in-place (OIP) and gas-in-place (GIP) is critical for evaluating shale oil and gas plays. Any loss of gas and condensate in transfer of cores from the subsurface to well site significantly affects the estimate of *in-situ* oil or gas saturation. Nano-size pores are typically host methane in low permeability mudstones, and the presence of pores that are filled with oil and gases but isolated with surrounding mineral matrix is highly possible. A rock crushing experiment has been devised to test for the presence of gas and condensate in isolated nanopores. A gas-tight rock crushing cell has been developed which can directly introduce the released gas to GC after crushing. We have tested this method on core samples of the Eagle Ford Formation, TX, USA.

Five core samples with burial depth from 4758ft to 13608ft collected from organic-rich lower Eagle Ford unit were used in our study. TOC content is from 1.8% to 8.5%, and Tmax value is from 428°C to 543°C. The calculated *Rc* based on Tmax value is from 0.5% to 2.6%, covering a wide range of thermal maturity. For comparison purpose, nine core samples with burial depth from 1250ft to 7223ft from organic-rich Barnett shale were used as well. TOC content is from 3.3% to 7.9%, and thermal maturity covers a wide range from 0.58% to 2.07% Ro.

Our results show that CH_4/CO_2 ratios are lower at low thermal maturities and much higher at high thermal maturities because more CH_4-rich gas is generated at high maturity levels. CH_4/CO_2 ratios decrease with longer rock crushing time because of increasing CO_2-rich adsorbed gas contribution. Both thermal maturity and gas desorption contribute to changes in CH_4/CO_2 ratio of released gas from rock crushing. However, no obvious compositional fractionation occurs among C_1, C_2 and C_3 in rock crushing, and C_1/C_2 and C_2/C_3 ratios keep nearly constant through crushing but greatly increase when the level of thermal maturity is high. Gas geochemical parameters (C_1/C_2, iC_4/nC_4) of released gas in rock crushing are good indicators of thermal maturation of organic-rich shales. CH_4/CO_2 ratio is proposed to identify the free gas and adsorbed gas contribution.

The carbon isotopes of methane, ethane, propane and carbon dioxide were measured for released gas from rock crushing. The $\delta^{13}C$ values of methane, ethane, propane and carbon dioxide become more positive with longer crushing time, indicating enrichment in ^{13}C heavy carbon isotope in adsorbed gas. The combination of gas compositional and carbon isotopic change might provide a way to differentiate and quantify the contribution of adsorbed gas and free gas in shale gas system.