

## **Measuring carbon isotope fractionation of methane during progressive degassing: a novel online GC-C-IRMS technique**

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Efficient exploitation of shale reservoirs depends on an understanding how gas is stored at pore scale within the shale: in macro and micropores, adsorbed onto pore surfaces or absorbed into the matrix of solid shale components. We hypothesise that carbon isotopic fractionation of methane during progressive depressurization can be used as a geochemical marker for gas stored in different sites within the shale, cumulating in more accurate total gas in place calculations.

We developed a custom-built sample cell and online gas chromatography – combustion – isotope ratio mass spectrometer (GC-C-IMRS) system to study methane isotope fractionation during depressurization. Effects of shale mineralogy on carbon isotope fractionation of methane were explored using samples representing key shale constituents; kaolinite, montmorillonite, calcite, quartz, marine kerogen and anthracite coal.

Matrix mineralogy was identified as a key control on isotopic fractionation. Each specific mineral group produces its own distinct carbon isotope fractionation trend. For example, high surface-area minerals such as clays display significantly greater isotope fractionation during depressurization than calcite. Our precise data ( $\pm 0.5\text{‰ } 2\sigma$ ) illustrate that this method reveals key gas-shale interactions.

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