Compound-specific Carbon and Hydrogen Stable isotope Ratios of Coalbed Gases in Southeastern Illinois Basin

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From field work to lab work:

Drilling site, SW Indiana, Seelyville coal, depth 100-200 m, R_r ~ 0.6%

Coal core

Immediate transfer of coal core segments into desorption canisters in the field

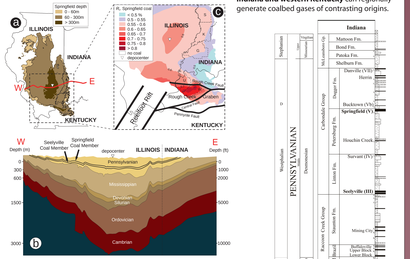
Desorption canisters

Volumetric determination of desorbed gas in the lab

Dariusz Strąpoć

(1) Geologic setting:

Stratigraphically equivalent and geographically widespread **coal beds of Pennsylvanian age in Indiana and western Kentucky** can regionally generate coalbed gases of contrasting origins.

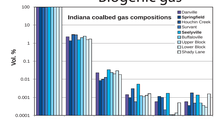


Above: Study area: (**a**) map of Springfield Coal Member depth; (**b**) East-West stratigraphic profile across Illinois Basin (along line indicated in Fig. 1a) with 52× vertical exaggeration; (**c**) map of vitrinite reflectance R_o of Springfield Coal Member overlain by major tectonic structures in southeastern Illinois Basin (after Greb et al., 1992; Hower et al., 2005) and dashed border lines of counties sampled for coalbed gases: S – Sullivan Co., K – Knox Co., G – Gibson Co., U – Union Co., W – Webster Co.

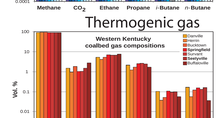
Above: Litostratigraphic column of Pennsylvanian in the Indiana part of Illinois Basin, with positions of sampled coal beds (modified from Mastalerz and Harper, 1998).

(2) Gas composition:

Biogenic gas



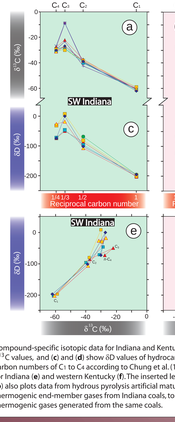
Thermogenic gas



Major gas components of coalbed gases in SE Illinois Basin. Note the logarithmic Y-axes. **Biogenic and thermogenic gases are compositionally very different.**

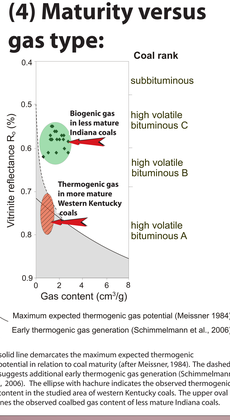
(3) Isotopic composition:

Large and systematic compound-specific hydrogen ($^2H/^1H$ ratio expressed as δD values) and carbon ($^{13}C/^{12}C$ ratio expressed as $\delta^{13}C$ values) stable isotopic differences between coalbed gases from Indiana and Kentucky reflect **fundamentally different gas origins and biogeochemical conditions**.



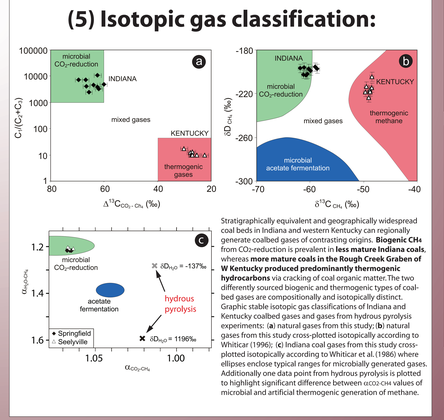
Compound-specific isotopic data for Indiana and Kentucky coalbed gases: (**a**) and (**b**) show $\delta^{13}C$ values, and (**c**) and (**d**) show δD values of hydrocarbons plotted against the reciprocal carbon numbers of C_1 to C_4 according to Chung et al.(1988). The same data are cross-plotted for Indiana (**e**) and western Kentucky (**f**). The inserted legend in (**f**) is valid for all panels. Section (**b**) also plots data from hydrous pyrolysis artificial maturation experiments that generated thermogenic end-member gases from Indiana coals, to compare artificial and natural thermogenic gases generated from the same coals.

(4) Maturity versus gas type:



The solid line demarcates the maximum expected thermogenic gas potential in relation to coal maturity (after Meissner, 1984). The dashed line suggests additional early thermogenic gas generation (Schimmelmann et al., 2006). The ellipse with hachure indicates the observed thermogenic gas content in the studied area of western Kentucky coals. The upper oval outlines the observed coalbed gas content of less mature Indiana coals.

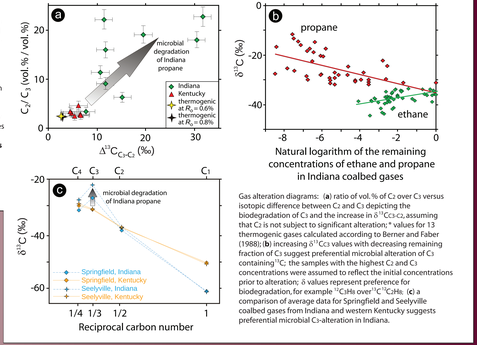
(5) Isotopic gas classification:



Stratigraphically equivalent and geographically widespread coal beds in Indiana and western Kentucky can regionally generate coalbed gases of contrasting origins. **Biogenic CH_4** from CO_2-reduction is prevalent in **less mature Indiana coals**, whereas **more mature coals in the Rough Creek Graben of W Kentucky produced predominantly thermogenic hydrocarbons** via cracking of coal organic matter. The two differently sourced biogenic and thermogenic types of coal-bed gases are compositionally and isotopically distinct. Graphic stable isotopic gas classifications of Indiana and Kentucky coalbed gases and gases from hydrous pyrolysis experiments: (**a**) natural gases from this study; (**b**) natural gases from this study cross-plotted isotopically according to Whiticar (1996); (**c**) Indiana coal gases from this study cross-plotted isotopically according to Whiticar et al. (1986) where ellipses enclose typical ranges for microbially generated gases. Additionally one data point from hydrous pyrolysis is plotted to highlight significant difference between $\alpha_{CO2-CH4}$ values of microbial and artificial thermogenic generation of methane.

(6) Biodegradation of Indiana C_{2+} coalbed gases:

Although most coal-bed gas in Indiana is CH₄ of microbial origin, small contributions of thermo-genic C_{2+} have been measured. C_{2+} hydro-carbons are are being degraded by microbes. Microbial biodegradation of thermogenic C_{2+} hydrocarbon gases in coal beds **preferentially targets C_3** and introduces isotope fractionation whereby **remaining C_3 is enriched in heavy isotopes** D and ^{13}C.



Gas alteration diagrams: (**a**) ratio of vol. % of C_2 over C_3 versus isotopic difference between C_2 and C_3 depicting the biodegradation of C_3 and the increase in $\delta^{13}C_{2-3}$, assuming that C_2 is not subject to significant alteration; * values for 13 thermogenic gases calculated according to Berner and Faber (1988); (**b**) increasing $\delta^{13}C_3$ values with decreasing remaining fraction of C_3 suggest preferential microbial alteration of C_3 containing ^{13}C; the samples with the highest C_2 and C_3 concentrations were assumed to reflect the initial concentrations prior to alteration; δ values represent preference for biodegradation, for example $^{12}C_3H_8$ over $^{13}C^{12}C_2H_8$; (**c**) a comparison of average data for Springfield and Seelyville coalbed gases from Indiana and western Kentucky suggests preferential microbial C_3-alteration in Indiana.

(7) Holocene water in coal beds:

The modern (Holocene) isotopic characteristics of waters associated with Indiana coal beds suggest that the residence time of water is less than 10,000 years. Fast fluid turnover in the presence of (i) abundant coalbed methane and (ii) methanogens in coal waters suggests that biogenic methane in Indiana coal beds may be continuously forming today. Indiana coal bed-associated waters are isotopically different from Mississippian and Pleistocene environmental waters. Data sources: [1]Craig (1961), Rozanski et al. (1993); [2]Stueber and Walter (1994); [3]McIntosh and Walter (2005); [4]McIntosh et al. (2002).

References:

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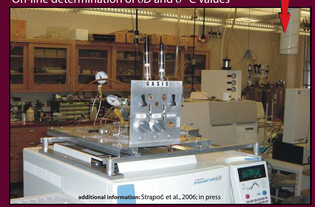
Stable isotope work:

Gas sub-sampling

Off-line preparation for δD_{CH4} and $\delta^{13}C_{CH4}$ analyses

On-line determination of δD and $\delta^{13}C$ values



Delta Plus XP mass-spectrometer and GASIS interface for gas inlet