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**Carbon and Hydrogen Isotope Systematics in Thermogenic Natural Gases from the USA  
and China: West meets East**

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Since the early pyrolysis work of Sackett (1978) we know that hydrogen isotopes behave the same way as carbon isotopes during thermal decomposition of kerogens, meaning that the fractionations of both isotopes are controlled by temperature. As a consequence hydrogen isotopes in thermogenic gases should behave as the theory predicts for carbon isotopes i.e. the isotopic difference between C1 to C4 gas molecules should decrease with increasing temperature (maturity) and the precursor-product fractionation decreases with the chain length of the molecule (Sundberg and Bennett, 1983, Tang et al. 2000). We can explore the combined use of carbon and hydrogen isotopes in natural gases using C and H isotope data from the US and China that became recently available (Liu et al. 2008a,b, Burrus and Laughrey, 2010, Ferworn et al., 2010, Schoell et al. 2010, Schoell unpublished).

The Bakken Shale gas data (Schoell et al. 2010) can serve as template for the behavior of carbon and hydrogen isotopes in oil-associated gases during maturation: the source of the gases is identical and isotopically uniform and the associated source kerogens exhibit a range of maturity as indicated by the variation of Hydrogen Indices with HI~170 to 530mg/g suggesting significant variations in conversion of kerogen to oil (Fig. 1a). As the gases are recovered from within the source rock, they are indigenous and have not mixed with other gases or have been altered by migration. Carbon and hydrogen isotopes in the Bakken gases are well related to the conversion of kerogen i.e. paleo-temperatures. With the exception of methane, C2 and C3 isotopes and their differences are well correlated with conversion (Fig.1b). Consequently we find the same isotope patterns in carbon and hydrogen isotopes of C1 to C4 gas components (Fig. 1c and d) proving that hydrogen isotopes in thermogenic gases are controlled by the same fundamental processes that were established for carbon isotopes.

Comparing C1 and C2 carbon isotopes of the Bakken gases (1 in Fig. 2a) with a large variety of gases from the US and China, it is surprising how small the carbon isotope variations are (Fig. 2a). Using the maturation trends for marine (KII) and terrestrial kerogens (KIII) as a guide we find most gases to plot below these maturation trends. There are two processes that could explain these patterns i) mixing of post-mature low C2+ gases with low mature gases high in C2+ (Jenden et al.,1993, see 4 in Fig. 2a) and ii) high mature shale gases that where exposed to high temperatures in quasi closed-system conditions (“rollover” of Ferworn et al. 2010, see 2 in Fig. 2a). It is clear that reverse isotope patterns in gases can be explained by mixing, as has been shown already by Jenden et al (1993). This mixing process was also inferred by Xu et al. (1997) to be an important process in many gas provinces in China.

Hydrogen isotope variations of methane and ethane in Bakken gases exhibit a clear maturation trend (Fig. 2b). Using the Bakken gases as template, we can infer similar maturation

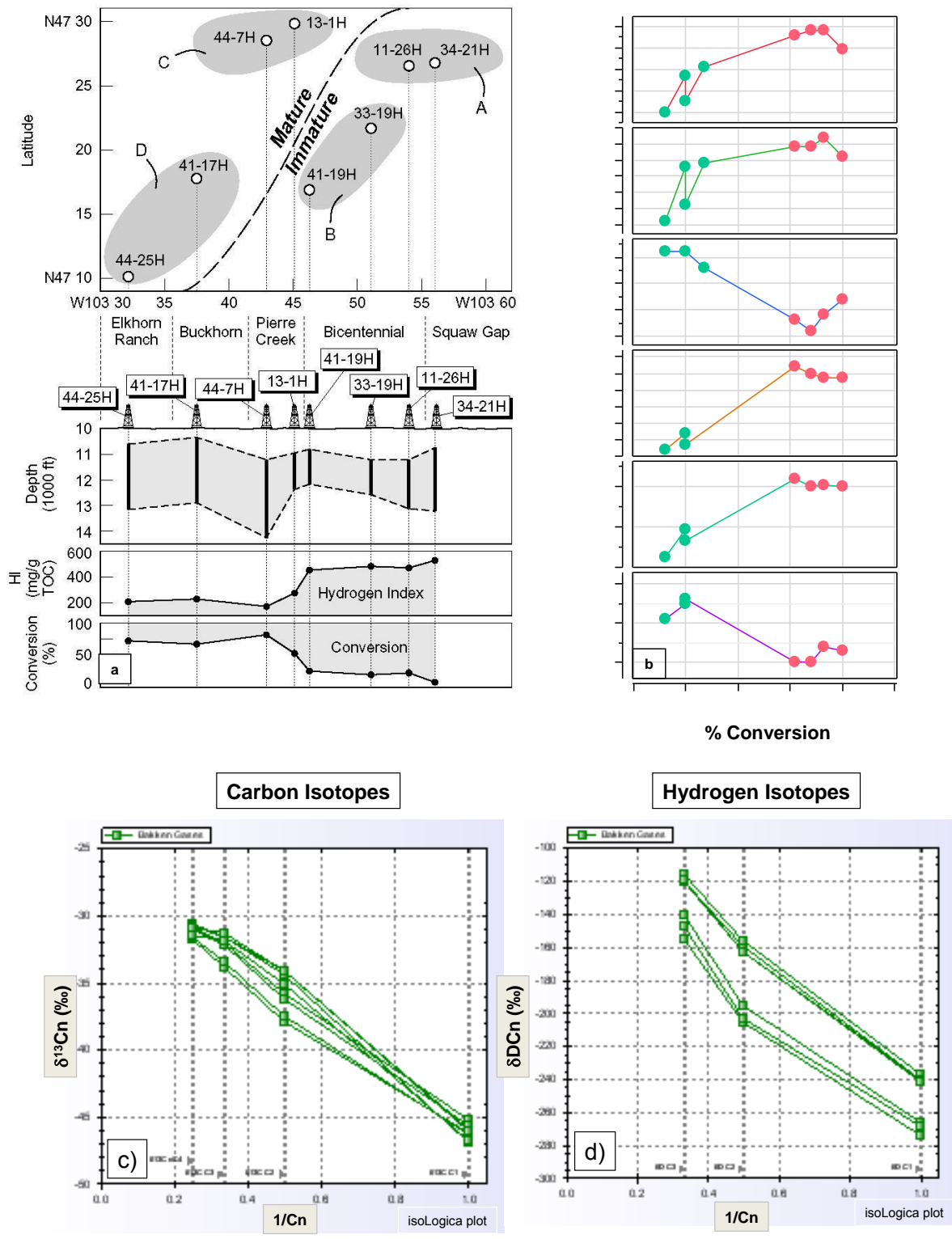
trends in other basins. Also mixing trends similar to those we used for carbon isotopes could be inferred.

A carbon isotope difference plot (Fig. 2c) supports the notion that maturation and mixing are the major processes controlling the isotope variations in natural gases. Exceptions are the super-mature Appalachian gases (Burrus and Laughrey 2010). Data variations in the same difference plot for hydrogen isotopes are less clear and need a deeper understanding of the processes that control hydrogen isotopes apart from mixing and maturation. Hydrogen isotope exchange does not occur in gases under normal maturation temperatures (Schoell 1984) and is therefore an unlikely explanation.

A topic for further research needs to be the effect of the kerogen type on hydrogen isotopes in C1 to C4 gas components. Schoell (1980, 1984) showed for methane that type II and Type III kerogens can be differentiated with carbon isotopes but NOT with hydrogen isotopes. This would mean that methane hydrogen isotopes are primarily controlled by maturity and are not source-specific. However, Liu et al. (2008) found C2-C3 hydrogen isotope differences for coal and oil-related gases. Controlled pyrolysis experiments and a theory for hydrogen isotope fractionations from different precursors, similar to that for carbon isotopes (Tang et al. 2000) would be required for a better understanding of hydrogen isotopes in natural gases.

## References:

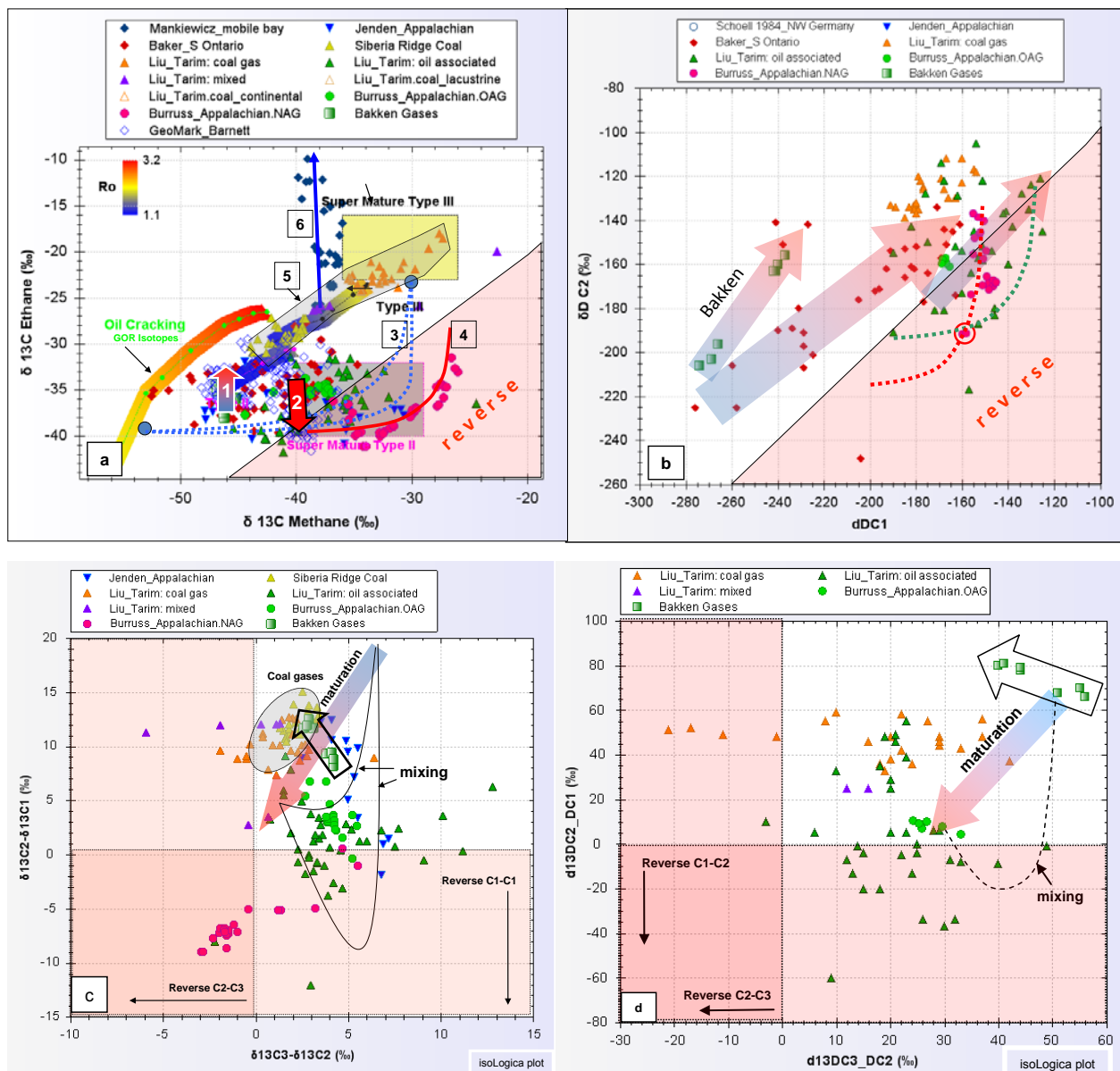
- Barker, J.F. and S.J. Pollock, 1984, *Bull. Can. Petrol. Geol.* 32, 313-326.  
Burrus, R.C. and Laughrey, C.D., 2010, *Org. Geochem.* 41, 1285-1296.  
Dai J. et al., 2004, *Org. Geochem.* 35, 405-411.  
Ferworn K., 2010, *Shale Gas Isotope Rollover* (Pers.comm. Geomark Data)  
Jenden P.D. et al., 1993, *AAPG Bull.* , 980-998.  
Liu et al., 2008, *Sci. China Ser D-Earth*, 51, 300-311 (Springer)  
Liu et al., 2008, *Earth Science Frontiers* 15, 209-216 (Springer)  
Mankiewicz et al. 2009\_ *AAPG Bull.* 93,1319-1346  
Sackett, W.M., 1978, *Geochim. Cosmochim. A.* 42, 571-580.  
Schoell M. (1980) *Geochim. Cosmochim. A.* 44, 649-661.  
Schoell M., 1984, *Geol.Jb. D67*, Schweizerbart, Hannover.  
Schoell M. et al. 2010, *AAPG/SEG/SPE/SPWLA Hedberg Conference*, Austin TX. Abstr.  
Sundberg K.R. and Bennet C.R., 1983, *Adv. Org. Geochem* 1981, 799-774, Wiley.  
Tang Y. et al. *Geochim. Cosmochim. A.* 64, 2673-2687.  
Xu S. et al., 1997, *Journal of Asian Earth Sciences* 15, 89-101



**Figure 1**

Carbon and hydrogen isotope systematics in Bakken shale gases

- a) Location of horizontal wells with Hydrogen Index and %Conversion of Kerogen
- b) Carbon and hydrogen isotopes of oil-associated C2 to C4 gases related to %conversion
- c) and d) Chung plots for carbon and hydrogen isotopes



**Figure 2**

Carbon and hydrogen isotope variations in natural gases from the US and China

- Carbon isotopes of methane and ethane
  - Bakken Shale
  - Super mature gases from the Barnett Shale (GeoMark “Rollover” Ferworn pers. Comm.)
  - Mixing trends for Appalachian gases (Jenden et al. 1993);
  - Mixing trends for Appalachia NAG gases (Burrus et al. 2010)
  - Coal Gases
  - in-reservoir cracking (Mankiewicz et al. 2009). Siberia Ridge data (Schoell, unpublished)
- Hydrogen isotopes of methane and ethane. Arrows are inferred maturation trends analog to those in the Bakken shale. Indicated mixing trends are inferred.
- Carbon isotope difference plot after Jenden et al. (1993)
- Hydrogen isotope difference plot with inferred mixing and maturation processes analogue to 2c