

## Unconventional generation of hydrocarbons in petroleum basin: the role of siderite/water interface

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Hydrocarbons in the petroleum basin of Solimões in Northern Brazil show isotopic trends similar to those of abiotic hydrocarbons observed in oceanic hydrothermal systems.

High concentrations of ferrous iron in the brines indicate a highly reduced environment. Such redox conditions are consistent with the large amount of siderite  $\text{FeCO}_3$  in the sediments. The capacity of siderite-water interactions to generate unconventional hydrocarbons has been tested experimentally.

Synthetic  $\text{FeCO}_3$  and water were reacted in gold containers at 500 bars, 200°C and 300°C. Siderite dissolution led to reducing conditions due to magnetite formation. In addition, at 200°C, TEM showed the precipitation of a nanometric layer of amorphous carbon covering magnetite grains. At 300°C,  $\text{H}_2$  was produced and reacted with  $\text{CO}_2$  to generate organic compounds such as methane and carboxylic acids [1]. The dissolved organic compounds concentrations are consistent with a cascade of reduction from  $\text{CO}_2$  to  $\text{CH}_4$  [2].

Alternatively,  $\text{CH}_4$  could form through the hydrogenation of the amorphous carbon coating observed on magnetite grains. This latter mechanism is more consistent with the isotopic data from the Solimões basin where, in addition, senile kerogen and  $\text{H}_2$ -rich fluids coexist. Experimental validation is currently underway.

[1] McCollom (2003), *Geochim. Cosmochim. acta*, **67**, 311-317. [2] Seewald *et al.* (2006), *Geochim. Cosmochim. acta*, **70**, 446-460.

## A new calibration of the carbonate clumped isotope thermometer based on synthetic calcites

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Previous calibrations of the clumped isotope thermometer based on synthetic calcites differ in the inferred relationship between isotopic ordering in the carbonate and temperature [1, 2]. The “absolute reference frame” proposed by Dennis *et al.* [3] improved the interlaboratory comparison but did not eliminate the discrepancies between the laboratories. It is clear that especially for inorganically precipitated carbonates more experimental data are needed. Here we present a new calibration on synthetic calcites and compile all published calibration data available to date.

Our new calibration is based on 11 synthetic calcites precipitated at known temperatures between 4°C and 80°C.  $\text{CaCO}_3$  was precipitated inorganically by mixing solutions of  $\text{NaHCO}_3$  (0.1M) and  $\text{CaCl}_2$  (0.1M) at the desired temperatures. The solutions were kept at known temperatures in incubators for 5 days before starting the experiments. Analyses were conducted at ETH on small carbonate samples (ca. 170-220  $\mu\text{g}$ ) using a Kiel IV Carbonate Device coupled to a Thermo Finnigan MAT 253 Mass Spectrometer [4]. The samples were measured multiple times on different days, with each measurement consisting of 9-15 analyses of separate aliquots. Data are presented relative to the “absolute reference frame” [3].

We find a robust linear relationship between  $\Delta_{47}$  and temperature of precipitation. We discuss several issues related to the slope of the linear regression through  $\Delta_{47}$  plotted against solution temperatures and the compilation of previous calibrations in the absolute reference frame.

[1] Ghosh *et al.* 2006. *Geochim Cosmochim Acta* 70, 1439-1456 [2] Dennis and Schrag, 2010. *Geochim Cosmochim Acta* 74, 4110-4122 [3] Dennis *et al.*, 2011. *Geochimica Et Cosmochimica Acta* 75, 7117-7131 [4] Schmid and Bernasconi, 2010. *RCMS* 24, 1955-1963.