

## Methane production and evolution within the crystalline basement

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CH<sub>4</sub>, along with H<sub>2</sub> and other reduced gases, is produced in significant quantities within the Precambrian crystalline basement [1]. However, the mechanisms, rates and temporal evolution of these deep crustal hydrocarbons are poorly constrained. While bulk isotope measurements ( $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$ ) remain a primary tool, multiple abiogenic and biogenic processes can affect and overprint the original signals, challenging interpretations. New developments in high resolution mass spectrometry have allowed measurement of low abundance doubly-substituted methane species (<sup>13</sup>CH<sub>3</sub>D & <sup>12</sup>CH<sub>2</sub>D<sub>2</sub>) [2]. Through comparison with abundances predicted by a purely stochastic distribution, the degree of ‘clumping’ can be calculated to provide insight into the processes controlling CH<sub>4</sub> in the deep crust [3].

Here we investigated the geochemistry of gases such as CH<sub>4</sub> and N<sub>2</sub> sampled from the 2.7 Ga crystalline basement in the Sudbury Basin in Canada. Gases sampled from this locality are distinctly different in composition, compared to all other gases described to date in Precambrian Shield systems, whether in Canada, South Africa or Fennoscandia. Typically compositions are dominated by N<sub>2</sub> and He (up to 50 % & 30 %) respectively, with much lower H<sub>2</sub>, CH<sub>4</sub> and heavier hydrocarbon concentrations than typically found elsewhere [1].

Like other sites examined to date, there is evidence for mixing between abiogenic (Fischer-Troph-type synthesis) and microbial CH<sub>4</sub>, but the microbial end-member may be significantly different than the CO<sub>2</sub> reduction-derived CH<sub>4</sub> typically seen at other sites [1]. Recent meta-proteomic and –transcriptomic work has shown that subsurface metabolic networks may be considerably more varied and complex than previously thought, including both microbially mediated methanogenesis and methanotrophy [3]. CH<sub>4</sub> isotopologue signatures at Sudbury share similar characteristics to samples from Kidd Creek interpreted to result from microbial methane cycling in deep fracture water ecosystems [2]. Measurements of doubly-substituted CH<sub>4</sub> isotopologues enable investigation of microbial methane cycling at this new locality.

[1] Sherwood Lollar et al. (2008) *GCA* **72** 4778-4795. [2] Young et al. (2017) *GCA* **203** 235-264. [3] Lau et al. (2016) *PNAS* **113** 7927-7936.