

## Examining pathways of hydrocarbon gas generation in Guaymas Basin hydrothermal sediments

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C<sub>2</sub>-C<sub>5</sub> hydrocarbon gases in organic-rich hydrothermal sediments of the Guaymas Basin exhibit unusual <sup>13</sup>C enrichment, with hydrothermal endmember δ<sup>13</sup>C values of up to -13 ‰ for ethane, followed by successively more negative δ values for propane, butane and pentane. Such a reversed (and isotopically heavy) C<sub>2+</sub> isotope pattern is atypical for thermogenic hydrocarbon gases and cannot be exclusively explained by post-genetic oxidation [e.g., ref.1] or mixing of gases in these sediments. Here, we explore whether catalytic reduction of volatile fatty acids (VFAs) could be a process to explain the isotope reversal and corresponding heavy hydrocarbon δ<sup>13</sup>C values in the highly reducing hydrothermal sediments of the Guaymas Basin. Using hydrous pyrolysis experiments at 250 to 350°C and 400 bars, we could show that in a two-step process: (1) exchange of carboxyl carbon of VFAs with <sup>13</sup>C-labeled bicarbonate occurred under hydrothermal conditions, confirming a previous hypothesis that this is a plausible process to cause <sup>13</sup>C-enriched VFAs [2], and (2) under reducing conditions, <sup>13</sup>C-labeled acetate was reduced, among other products, to ethane. Our findings indicate reduction of VFAs as a novel formation pathway of hydrocarbon gases in organic-rich sediments under highly reducing hydrothermal conditions.

[1] Cruse AM & Seewald JS (2006) *Geochim. Cosmochim. Acta* 70(8):2073-2092. [2] Franks SG, et al. (2001) *Geochim. Cosmochim. Acta* 65(8):1301-1310.