Bulk and clumped isotopic signatures of aerobically produced methane

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The discovery that certain aerobic bacteria could produce methane (CH_4) has served to explain the long-term puzzle of supersaturated concentrations observed in the world's surface oceans and has revolutionized the previous consensus that methane could solely be produced by anaerobic methanogenesis [1]. The release of CH_4 by specific aerobic bacteria has been shown to occur in oxygen-rich, phosphate-starved ecological niches that characterize large areas of Earths oceans and some lakes. These microbes are able to alternatively derive P by breaking down organic matter bound phosphonates, particularly methylphosphonate (MPn) [1,2]. Through the metabolic decomposition of MPn, methane is released as a by-product. The release of this potent greenhouse gas in P-starved surface oceans may signficantly contribute to the atmospheric methane budget.

This study is developing a comprehenensive isotopic fingerprint of the stable isotopic fractionations upon MPn degradation to CH_4. Using pure cultures of representative organisms, we determine the bulk $^{13}C/^{12}C$ and $^{2}H/^{1}H$ compositions, as well as the novel clumped isotopic metrics: $^{12}CH_2D_2$ and $^{13}CH_3D$. Initial results show that methane produced during MPn degradation shows little to no fractionation from the substrate in bulk $^{13}C/^{12}C$ values, and some depletion from medium water $^{2}H/^{1}H$. Preliminary clumped isotope values suggest that this production mechanism likely produces CH_4 that is distinct from the canonical anaerobic methanogenesis pathways.

The enzyme utilized to break the carbon-phosphorous bond that ties the $P^{(3+)}$ in MPn, the C-P lyase, has been identified in numerous key marine microbes, including strains of *Trichodesmium erythraeum, Pelagibacterales* (SAR11), and the strain studied herein *Pseudomonas stutzeri* HI00D01, indicating that phosphonate breakdown coupled to methane production is possible throughout parts of surface oceans [1,2]. This work presents the potential to identify a unique process-specific set of stable isotopic fractionation factors for aerobic methane production.

[1] Repeta et al., (2016) Nature Geoscience 9, 884-887.
[2] Carini et al., (2014) Nature Communications 5, 4346.