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Methane clumped isotopes reveal the formation of microbial methane

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Methane is a key component of global biogeochemical cycles and a primary target in astrobiological investigations. Strong isotopic discrimination during methane formation has driven the extensive application of carbon and hydrogen isotopes in distinguishing microbial from thermogenic and abiotic methane, as well as in facilitating the construction of global methane budgets. The recent utilization of doubly substituted “clumped” isotopologues has emerged as a novel tool for characterizing sources and sinks of methane. Microbial methane often displays isotope and isotopologue disequilibrium in shallow terrestrial environments but near-equilibrium signals in deep marine sediments. The origin of this near-equilibrium methane, whether directly produced by methanogens or achieved through anaerobic oxidation of methane (AOM), remains uncertain.

Here, we analyzed the methane clumped isotopologue compositions of natural methane gas samples from diverse systems, including boreal lakes, coastal wetlands, and deep-sea basins, where methanogenesis exceeded AOM. Subsequently, we performed laboratory incubations to study methanogenesis in these sediments, amended with inhibitors to limit AOM activity but without alteration of the natural substrate concentration. Our findings show that methanogens in deep-sea sediments generate methane in both intra- and inter-species isotope equilibrium under both natural and laboratory conditions, without experiencing methane oxidation. The limitation of free energy resulting from recalcitrant organic matter promotes high metabolic reversibility in deep-sea sediments. In contrast, methane from coastal wetlands and boreal lakes, where the organic matter is more labile than deep-sea sediments, exhibits significant hydrogen and clumped isotope disequilibrium.

Combining with previous research, we suggest that the near-equilibrium methane isotopologue signatures result from intracellular isotope exchange operating under conditions of near-threshold free-energy that is catalyzed by methyl-coenzyme M reductase, allowing for either net methanogenesis or AOM. When the thermodynamic driving force is elevated, methanogenesis and AOM can generate more negative and positive isotopologue signatures, respectively. Methane clumped isotopes therefore emerge as a valuable tool to trace anaerobic methane metabolisms in natural settings, potentially serving as interplanetary biosignatures. Future space missions could benefit from additional research and technique development for in-situ mission measurements of methane clumped isotopes on Mars, Enceladus, and other solar system bodies, where methane cycling is considered a key (bio)geochemical tracer.