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Kilometer-scale profiles of $\delta^{13}CH_3D$ distinguish end-member mixing from methane production in deep marine sediments

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Methane stored in marine sediments can be formed by microbially- and/or thermally-mediated decomposition of organic matter. Identifying sources of methane allows the potential of natural gas reservoirs and the limits of microbial life in subsurface environments to be assessed. However, such assessments are complicated by the burial and advective transport of methane, which can produce mixtures from mutliple sources. We measured the abundances of stable isotopes ($^{13}C/^{12}C$ and D/H), clumped isotopologue ($^{13}CH_3D$), and low molecular weight hydrocarbons (C_1/C_{2+3}, the ratio of methane over ethane plus propane) for gas samples collected by mud-logging during seafloor drilling to test if $^{13}CH_3D$ provides additional constraints about the source(s) of methane. Two depth profiles spanning several kilometers of sediment and representing the transition between prominent microbial and thermal methanogenic zones were analyzed. Samples from the northeastern Gulf of Mexico are from 1619 to 3271 mbsf (sediment temperatures from ca. 46 to 96°C), and samples from the western Black Sea are from 2170 to 3990 mbsf (sediment temperatures from ca. 105 to 183°C). We found that $\delta^{13}CH_3D$ values of methane do not follow simple two-component mixing between shallow microbial and deep thermogenic end-members. Our data suggest that methane isotopologues re-equilibrate along geothermal gradients as methane is buried. The re-equilibration may be microbially catalyzed, as abiotic isotopologue exchange is slow at temperatures less than ca. 150°C. The equilibration appears to continue until the temperature reaches 100±10°C, which is ca. 20° higher than the previously suggested upper temperature limit of microbial methanogenesis in marine sediments. At temperatures above 150°C, methane isotopologues equilibrate abiotically on a timescale of 10s of millions of years or less. Off-sets between isotope-based temperatures and estimated in-situ sediment temperatures indicate the importance of upward advection in the northeastern Gulf of Mexico, and burial in the western Black Sea. This study provides novel kilometer-scale profiles of clumped methane isotopes in marine sediments, and the means to trace the upper-temperature limits of microbial activity in hydrocarbon-rich marine sedimentary environments.