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The evolution of methane clumped isotope compositions during nitrite-dependent anaerobic methane oxidation

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Methane is an important energy source, a potent greenhouse gas, and a potential biosignature for extraterrestrial life. Therefore, it is crucial to understand the methane cycling in natural environments. On Earth, microbial methanotrophy composes a crucial part of the methane sink. Traditionally, microbial methanotrophy is categorized into the aerobic oxidation of methane (AeOM) and anaerobic oxidation of methane (AOM). Each microbial process utilizes different biochemical reactions and enzymes. AeOM is initiated by the methane monooxygenase (MMO) enzymes, while AOM uses methyl-coenzyme M reductase (MCR) for the initial step. Previous studies have shown that the evolution of methane clumped isotope compositions ($^{13}CH_3D$ and $^{12}CH_2D_2$) during AeOM and AOM are different (*1*, *2*) and thus can be used to distinguish these two processes in nature (*3*). In this study, we investigate how the clumped isotope compositions of methane evolved in a novel methanotrophic process, nitrite-dependent anaerobic methane oxidation (N-DAMO). We find that N-DAMO generates the isotopic signal of AeOM. This is evidently due to the fact that particulate methane monooxygenase (pMMO) is utilized in N-DAMO (*4*). We further investigated the temporal change of methane clumped isotope signatures in an experimental system where pMMO and MCR-mediated methane oxidation co-occur. We find the methane clumped isotope compositions potentially reflect the relative oxidation rates of the two processes. Our findings show that the different clumped isotope signatures of AeOM and AOM are simply manifestations of the oxidative enzymes at play. Additionally, this study shows the potential of methane clumped isotopes in probing the activity of MMO and MCR-mediated methane oxidation in natural environments. Furthermore, understanding signatures for biological versus abiotic methane destruction on Earth will aid our investigation of methane cycling elsewhere in the Solar System.

1. J. Li *et al.*, *Geochim. Cosmochim. Acta*, S0016703724003314 (2024).
2. J. Liu *et al.*, *Geochim. Cosmochim. Acta*. **348**, 165–186 (2023).
3. T. Giunta *et al.*, *Geochim. Cosmochim. Acta*. **338**, 34–53 (2022).
4. K. F. Ettwig *et al.*, *Nature*. **464**, 543–548 (2010).