

## Simultaneous determination of carbon and hydrogen isotope enrichment factors of methane during microbial oxidation in a natural water environment

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The stable carbon and hydrogen isotope compositions ( $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ ) of methane ( $\text{CH}_4$ ) were analyzed using a newly developed CF-IRMS method in a hydrothermal plume in the water column of Lake Towada, Japan. The  $\text{CH}_4$  concentration,  $\delta^{13}\text{C}\text{-CH}_4$ , and  $\delta^2\text{H}\text{-CH}_4$  in the lake water column varied widely, ranging from 0.6 to 246.5 nM,  $-54.9$  to  $+54.2\text{‰}$  (vs VPDB), and  $-258$  to  $+762\text{‰}$  (vs VSMOW), respectively, reflecting rapid  $\text{CH}_4$  oxidation in the water column. Rapid  $\text{CH}_4$  oxidation was further confirmed through bottle incubation experiments of the lake water sampled below 150 m, which found an extreme increase in the values of both  $\delta^{13}\text{C}\text{-CH}_4$  and  $\delta^2\text{H}\text{-CH}_4$  corresponding to a decreasing  $\text{CH}_4$  concentration, after the incubations of more than 48 hours. The isotope enrichment factors for carbon and hydrogen were determined through incubation experiments to be  $-26.2 \pm 0.9\text{‰}$  and  $-233 \pm 12\text{‰}$ , respectively, and the rapid rate constants ranged from 0.05 to 0.67  $\text{day}^{-1}$ . These enrichment factors were the highest values ever reported in natural environments. In addition, we found that a greater isotope fractionation occurred at larger rate constants, i.e., higher populations of  $\text{CH}_4$  oxidizing microbes. However, we also found that the ratios between the isotope enrichment factors of hydrogen and carbon ( $\Lambda$  values) were always constant around  $11.3 \pm 0.9$ , which coincides well with previous laboratory and field observations under elevated  $\text{CH}_4$  concentration. The coincidence in the  $\Lambda$  value of approximately 10 between this study and previous studies indicates that the  $\Lambda$  value can be a robust tracer for distinguishing microbial  $\text{CH}_4$  oxidation from the other processes such as mixing, even in environmental samples of nanomolar per liter quantities of  $\text{CH}_4$ .

## LIME Olivine and Pyroxene: Multi-Stage Thermal Histories of AOAs

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Low-iron, Mn-enriched (LIME) silicates are interpreted as indicators of nebular condensation conditions [1-4]. They have been identified in IDPs [1], in rare chondrules and matrices of primitive chondrites [2, 3], and in Wild 2 cometary grains [4]. LIME olivine has also been observed in amoeboid olivine aggregates (AOAs) in primitive chondrites [6, 7]. In this study, we compare the roles of nebular and asteroidal thermal processing on formation and alteration of LIME silicates in AOAs.

Most AOAs in Y-81020 (CO3.0) are compact, with closely intergrown minerals. The compact AOAs have concentric textures of anorthite  $\pm$  spinel cores, Al-diopside-rich mantles and closely-packed forsterite rims. Some AOAs appear to be more loosely-bound (fluffy). The fluffy AOAs have more irregular shapes, contain less Al-diopside and lack the well-defined concentric textures of the compact AOAs.

LIME olivines are commonly observed in AOAs in Y-81020. They typically occur (i) in the rims of compact AOAs, and (ii) as uniformly distributed grains in fluffy AOAs (see [7]). Most olivines in both types of AOAs are nearly pure forsterite ( $\text{Fo}_{99-100}$ ). LIME low-Ca pyroxenes are also observed in rims of some AOAs. Their MnO concentrations are similar to those of coexisting LIME olivines.

LIME olivine and pyroxene both occur in the rims of compact AOAs in Y-81020, consistent with a model calculation that predicts Mn-enrichment with decreasing condensation temperature in the nebula [5]. AOAs in metamorphosed type 3 carbonaceous chondrites apparently lack LIME silicates [8]. We suggest that LIME silicates were originally present as primary phases in many AOAs, and then were lost during asteroidal thermal processing.

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