

Carbon isotopes of CH₄ in Archean fluid inclusion: a new insight into methanogenesis on the early Earth

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Methane may have played an important role in controlling both surface temperature and atmospheric chemistry, especially during the Precambrian (e.g., Kasting and Catling, 2003). For the present, very little direct information is available on the concentration and origin of CH₄ in the Precambrian ocean and atmosphere. One possible approach for tracing the past gas phase is to study fluid inclusions, which contain gasses entrapped in crystallizing minerals. The carbon and hydrogen isotopes of fluid inclusion CH₄ have potential to determine its origin. In this paper, we report petrography and in-situ Laser Raman microspectroscopy of methane-bearing fluid inclusions preserved in ~3.5 billion-years-old (Ga) hydrothermal silica dikes from the North Pole area, Pilbara Craton, Western Australia. Also, we have developed analytical method to extract the trace amount of CH₄ by vacuum crushing, and determine its carbon isotopic compositions. The results of this study provided the following new observations: (1) The ~3.5 Ga silica dikes contain numerous primary fluid inclusions, which would have been entrapped during the growth of the host quartz, with various amount of secondary fluid inclusions. (2) The primary fluid consists mainly of H₂O and CO₂ with minor but detectable amount of CH₄. (3) The δ¹³C values of CH₄ and CO₂ are -56 to -36 permil and -7.4 to 0.0 permil, respectively. The difference of δ¹³C values between CH₄ and CO₂ (34 to 52 permil) are much larger than those in isotopic equilibrium at above 300 C. This indicates that the δ¹³C value of methane would not have changed significantly by thermal metamorphism. The variation of δ¹³C values of the methane can be explained by mixing of primary and secondary components, because the ¹³C-depleted CH₄ are preferentially observed in sample rich in primary inclusions, whereas less ¹³C-depleted CH₄ in those rich in secondary inclusions. The very negative δ¹³C value of the primary component (less than -56 permil) suggests that the CH₄ would be derived from bacterial methanogenesis. On the other hand, δ¹³C value (~ -36 permil) of the secondary component is similar to those of kerogens in the surrounding rock, suggesting its thermogenic origin. Bacterial origin of the primary component is consistent with the absence of higher hydrocarbons and similarity to expected δ¹³C values of bacterial CH₄ calculated from the isotopic compositions of coexisting CO₂ or surrounding organic matter. If the model is correct, this methane would be the oldest (~3.5 Ga) record of methanogenic activity.