

## Intra-molecular isotope analysis of acetate in a serpentinite-hosted hydrothermal system

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In serpentinite-hosted hydrothermal systems, hydrocarbons may be formed by Fischer-Tropsch-type (FTT) reactions catalyzed by mineral formed through serpentinization (e.g., Holm et al., 2001; Proskurowski et al., 2008; McCollom and Seewald, 2007). Furthermore, organic acids formate and acetate have been found in some serpentinite-hosted hydrothermal systems (e.g., Nothaft et al., 2021). However, the origin of these organic acids is still ambiguous. In this study, we report bulk and intramolecular carbon isotopic compositions of formate and acetate from the on-land serpentinite-hosted hot spring Hakuba-Happo, Japan. In order to measure trace amounts of the organic acids, formate and acetate were first concentrated using a rotary evaporator. The concentrated samples were extracted using Solid Phase Micro-Extraction (SPME) and injected into GC-C-Py-GC-IRMS (Yamada et al., 2014) for isotope analysis. The results revealed that the methyl position of acetate ( $\delta^{13}\text{C}_{\text{methyl}} = -27\text{‰}$  to  $-28\text{‰}$ ) was depleted in comparison to carboxyl position ( $\delta^{13}\text{C}_{\text{carboxyl}} = -13\text{‰}$  to  $-6\text{‰}$ ). The carboxyl carbon of the acetate is isotopically close to co-existing formate ( $-10\text{‰}$  to  $-11\text{‰}$ ) and to previously measured DIC ( $-7\text{‰}$ ; Suda et al., 2022). The results are consistent with an abiotic reaction in a highly reducing environment, where acetate would be formed from two isotopically distinct precursors: a  $^{13}\text{C}$ -depleted reduced precursor that would also form methane, and a  $^{13}\text{C}$ -enriched oxidized one that would form formate. However, the isotope difference between the methyl and carboxyl C-atoms of acetate are also in the range of those reported for biologically synthesized acetate (from 3 to 24 ‰; Blair et al., 1985). Therefore, a biological origin of acetate cannot be fully discarded. Future incubation experiments aiming at reproducing the production and consumption of acetate may be critical to understand its origin in serpentinite-hosted hydrothermal systems.