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In situ Raman quantitative monitoring of formate formation during carbon dioxide hydrogenation under hydrothermal conditions

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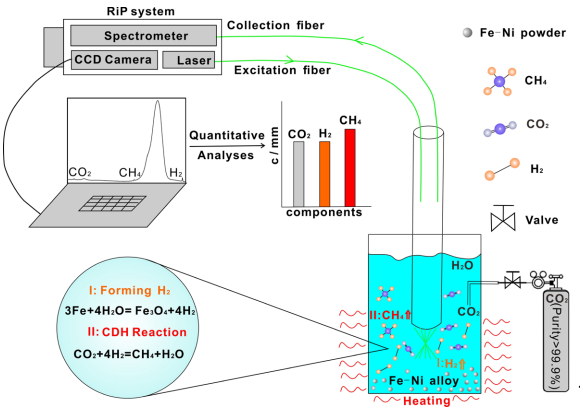

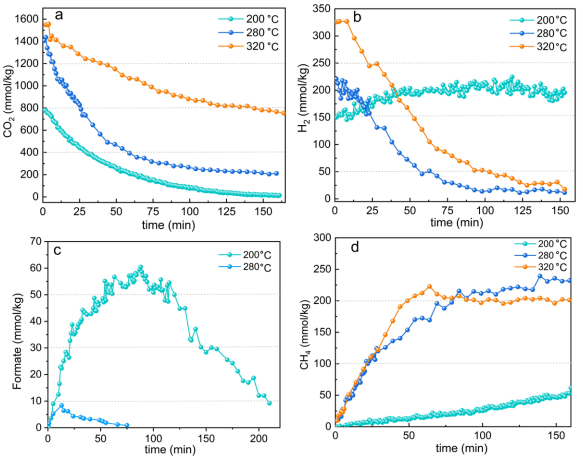

Formate ($HCOO^-$), which is crucial for microbial communities, has been widely detected in diverse high-temperature geological environments, including hydrothermal vent fields [1] and deep lithosphere [2]. However, previous studies suggest that carbon dioxide hydrogenation produces negligible or very low concentrations of formate. It remains unclear whether and how large quantities of abiotic formate can be generated through natural geological processes. Here the reaction of carbon dioxide (CO_2) with hydrogen (H_2) at 200-320 °C and 30 MPa was monitored using in situ Raman quantitative analysis technique (Fig.1). The concentrations of formate ($HCOO^-$) at low temperatures (≤230 °C) were several orders of magnitude higher than those reported in previous studies. At 200 °C, reduction of CO_2 to $HCOO^-$ proceeded rapidly during the first 80 min, and $HCOO^-$ concentrations reached a maximum value of 60 mmol/kg. Then, $HCOO^-$ concentrations decreased while CH_4 concentrations increased significantly. The final products at low temperatures (≤230 ℃) contained high concentrations of formate (Fig.2). The delayed CH_4 peak implies that a considerable amount of $HCOO^-$ may escape in an open environment. The proto-ocean was an open system with intense convections near hydrothermal vents, allowing for a significant amount of formate produced by carbon dioxide hydration to escape and be preserved in cold regions with temperatures ≤230 °C. This resulted in a formic acid-rich layer in the proto-ocean, promoting the polymerization of amino acids and the origin of life.

[1] Goldschmidt, Lang (2010), *Geochimica et Cosmochimica Acta* 74,941-952.

[2] Goldschmidt, Lollar (2021), *Geochimica et Cosmochimica Acta* 294, 295-314.