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In situ decarboxylation of acetic and formic acids in aqueous inclusions as a possible way to produce excess CH4

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Accurate reconstruction of diagenetic P-T conditions in petroleum reservoirs from fluid inclusion data relies on valid measurements of methane concentration in aqueous inclusions. Techniques have been developed (Raman spectrometry) to provide sufficiently accurate data, assuming measured methane concentration has not been modified after aqueous inclusion entrapment. In petroleum reservoirs, acetic (CH3COOH) and formic (HCOOH) acids are the most commonly reported organic acids, and the concentration of the total organic acids can be as high as 10,000 ppm at temperature below 120°C. This study investigates the likelihood that organic acids derived from petroleum fluids and dissolved in formation water might suffer decarboxylation upon post-entrapment heating within the fluid inclusion chamber upon post-entrapment heating, thereby generating excess CH4 in the inclusions. Four different experiments were conducted in Fused Silica Capillary Capsules (FSCCs), mimicking fluid inclusions. The capsules were loaded with acetic (CH3COOH) or formic (HCOOH) acid solution and were heated to 250°C for short durations (< 72hrs) in closed system conditions, with or without applying a fixed PH2. Reaction products were characterized by Raman and FT-IR spectrometry. The beginning of the decarboxylation of acetic acid is reached in 32 h at 250°C, with production of CH4 and CO_2. Complete decarboxylation of formic acid is reached in 5 h at 250°C, with production of CO_2, CO and H2. The lack of CH4 production in experiments with formic acid may be attributed to the relatively short duration of the experiments and/or the loss of H2 through the FSCC by diffusion during the experiment. Further experiments with a longer heating duration should be performed to assess the possibility of reducing the CO_2 into CH4 from the formic acid. 2) The injection of H2 in the FSCC as a way to promote CO_2 reduction did not promote decarboxylation in the duration of our experiment. These results suggest that methane may be produced from dissolved acetic acid in natural aqueous inclusions in specific situations, possibly inducing errors in the thermodynamic interpretation.