

Formation of hydrocarbons favors high pressure at subduction zones conditions: a study from in-situ experiments

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Subduction zones are geological settings which could be channels for carbon transport to the deep Earth. Inorganic and organic carbon in fluids released from the subducted slab are important in water-rock interactions. Field observations of CH₄-H₂ fluid inclusions in the ophiocarbonates in metamorphosed ultramafic rocks have shown the possible metastability of hydrocarbon fluids at upper mantle conditions[1]. In experiments, synthesized fluids of CH₄-C₂H₆-H₂ are trapped in quartz from Na-formate solution at 600-700°C and 1.5-2.5 GPa[2]. These studies suggest that pressure might be an important factor in the formation of hydrocarbons under the upper mantle conditions.

We focused on the role of pressure influencing the formation of hydrocarbons using diamond anvil cell experiments starting with 1.0 M Ca-acetate solutions over a wide range of pressures (1.5 – 4.6 GPa) at temperatures of 300 and 350 °C. Droplets of immiscible hydrocarbon fluid coexisting with aqueous carbonate or bicarbonate and crystals of calcite or aragonite were formed at peak pressure and temperature conditions in the experiments. Greater quantities of hydrocarbons formed at higher pressure as revealed by measuring the *in situ* volume percent of the droplets. Also, analysis of the Raman spectra of the aqueous solutions indicated that the reactions forming hydrocarbons were accelerated by high pressure.

In previous experiments starting with Na-acetate solutions[3], immiscible hydrocarbon droplets containing mainly methane and isobutane formed at 300 °C and 3.0 GPa. Compared to the previous Na-acetate experiments, this study found hydrocarbons that were more isobutane and propane-rich, but methane poor. In experiments at around 350 °C, aromatic hydrocarbons formed which caused strong fluorescence using a 532 nm laser. Increase of temperature is the main reason for forming aromatic hydrocarbons in our experiments. The dried aromatic hydrocarbons were measured using a UV laser, and show peaks of bitumen.

Progress in our experiments shows that the formation of hydrocarbons is closely related to higher pressures at the same temperature. Our study supports the possible co-occurrence of hydrocarbons and carbonate minerals in subduction zones.

[1] Brovarone et al.(2017), *Nature Communications* 8, 1-13.

[2] Li et al.(2017), *Geochemical Perspectives Letters* 3, 12-21.

[3] Huang et al.(2017), *Nature Communications* 8, 1-8.