Aqueous Acetate Coexisting with Immiscible Fluid Isobutane at Subduction Zone Pressures

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Acetate is a common aqueous species in buried sediments and may be food for a deep biosphere[1]. Low pressure studies of aqueous Na-acetate stability established decarboxylation to CH_4 and CO_2 at about 300-400°C[2]. However, recent theoretical studies[3] indicate that at P > 3.0 GPa, subduction zone fluids could contain aliphatic acids and aqueous hydrocarbons with inorganic C-species at equilibrium.

To experimentally investigate the effect of pressure on acetate stability, we studied ~1.0 M Na-acetate solutions in the diamond anvil cell using Raman spectroscopy at 300 ºC and 3.0 GPa for up to 60 hours. Part of the acetate initially decomposed to bicarbonate/carbonate species and methane, with no detectable H_2. However, within the first two hours of heating, immiscible droplets of C_2-C_4 hydrocarbons, mostly isobutane formed. Simultaneously, natrite (Na_2CO_3) crystals precipitated from the fluid. Both droplets and crystals persisted throughout the experiments. In the aqueous fluid, acetate and HCO_3^- were present during the first 6 hours, and CO_3^{2-} became important after 20 hours of heating. There was residual acetate at the end of the experiment. Stable final HCO_3^-/CO_3^{2-} and acetate/HCO_3^- ratios indicated a constant pH and achievement of a steady state. After decompression, a gas bubble in the cell consisted of methane (>90%) and ethane plus propane (<10%) by volume. Overall, the final molar distribution of C is istobutane (37%), C(IV) species (38%), methane (12%), and residual acetate (13%). The products from long (60 hr) and short-term (30 min) experiments suggested isobutane was produced either through polymerization or ketene mechanisms involving acetone. A preliminary thermodynamic model indicated the early production of methane that was partially consumed and dissolved in the hydrocarbon fluid.

We suggest that subduction zone fluids at high pressures might involve abiotically produced immiscible fluid hydrocarbon species as well as inorganic and organic aqueous C-species.

[1] Wellsbury et al. (1997), *Nature*, 388, 573-576. [2] Palmer and Drummond (1986), *GCA*, 50, 813-823. [3] Sverjensky et al. (2014), *Nat. Geosci.*, 7: 909–913.