The acidity of hydrothermal solutions on the ocean floor

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Hydrothermal solutions at submarine hydrothermal vents can be quite acidic. At mid-ocean ridges, pH values typically range around 3-5. In hydrothermal systems in back arc environments pH values appear to be more variable and are typically more acidic, likely reflecting the greater chemical and petrologic diversity of back arc environments compared with MORB settings. The lowest reported pH values, all from the Western Pacific region, range around 1 to 2 [1] [2].

Several reaction mechanisms are identified in being pH effective in hydrothermal solutions, including the degassing of SO_2 from a sub-surface magma source and its disproportionation in seawater; the exchange of cations in seawater by H_3O^+ with lithologies of the oceanic lithosphere by wall rock alteration; and the hydrolysis of salts with retrograde solubility that precipitate poorly soluble hydroxides during heating and extract hydroxyl from the solution.

To assess the role of hydrolysis of NaCl in acidifying hydrothermal solutions on the ocean floor, experiments are being carried out in titanium metal autoclaves along the two-phase curve of seawater, as well as in brines of the H_2O-NaCl system. Temperatures range from 250 to 390°C, Pressures are constrained by the two-phase curve and are a function of run temperature and electrolyte concentration of the brine. Brine and vapor are sampled *in-situ* separately and analyzed for pH and the major cations and anions in solution. Solid precipitates are identified by XRD. In both bulk compositions, the pH at 25°C of condensed vapor phases (pH_{25}) falls with increasing temperature and increasing electrolyte concentration in the brine, to as low as 2 in condensed vapor phases at 350°C in equilibrium with seawater. Apparently, NaCl hydrolyses significantly at elevated temperature. The HCl molecule is quite volatile and fractionates in the gas phase when hydrothermal solutions boil, while NaOH and NaCl remain in the brine. Na/Cl and Cl/Br ratios in vapor phases correlate stringently with pH_{25}. In seawater, the fractionation of HCl in the vapor phase is more pronounced than in the simple H_2O-NaCl system because seawater contains a number of other electrolytes that also undergo hydrolysis, precipitating solid hydroxides and adding to HCl in the vapor phase. Hydrolysis of NaCl is most effective in acidifying hydrothermal solutions when solutions boil within a hydrothermal vent, and probably the main reason why hydrothermal solutions can be so acidic.

[1] Gamo T. *et al*. (1997) *Geology* **25**, 139-142. [2] Reeves *et al*. (2011) *GCA* **75**, 1088–1123.