

Spectrophotometric Determinations of Carbonate Dissociation Constants in Seawater

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Carbonate system parameters (pH, total alkalinity (TA), total dissolved inorganic carbon (DIC), carbon dioxide fugacity (fCO₂)) are related through calculations involving the CO₂ dissociation constants, K₁ and K₂. These constants, which relate H⁺ concentrations to the relative concentrations of CO₂, HCO₃⁻ and CO₃²⁻, have uncertainties on the order of 2% and 5% respectively and thereby limit our understanding of the marine CO₂ system. The goal of my investigation is improvement of the accuracy of K₁ and K₂ parameterizations over a wide range of salinity and temperature.

My determinations of K₁ and K₂ are being performed using spectrophotometric pH measurements obtained with purified meta-cresol purple indicator. The procedure used in this work involves adjustments of solution pH to values near an expected equilibrium pH, and then adding pure NaHCO₃ to determine the pH at which NaHCO₃ additions produce no pH change. The pH at which NaHCO₃ additions cause no pH change is equal to $\frac{1}{2}(pK_1+pK_2)$. Calculated K₂ values and literature K₁ values will subsequently be used to determine whether the correspondence between calculated and measured TA, DIC and pH values obtained on the GOMECC-3 expedition (2017) is improved relative to calculations that use previous K₁ and K₂ parameterizations.