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Carbonic Acid Dissociation in Non-Standard Seawater: Implications for Carbonate Chemistry Reconstructions and Atmospheric CO2 Through Time

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The dissociation of carbonic acid in aqueous solutions such as seawater is critical to numerous processes in environments ranging from brackish waters to brines and to applications from ocean acidification to carbon sequestration and paleo-seawater reconstructions. In waters of standard major ion composition, the dissociation of carbonic acid is well understood. Moreover, the first and second stoichiometric dissociation constants of carbonic acid (K1* and K2*), necessary to constrain the carbonate system, have been well established in dilute solutions, NaCl media, and standard seawater. However, such constants have not been accurately measured in seawater of non-standard major ion composition, specifically concerning variations in [Mg2+], [Ca2+], and [SO42-]. Currently, K1* and K2* data are sparse in the literature for solutions of non-standard ion composition across temperature ranges (0-40 deg C) and ionic strength (0.25-6). However, such data are imperative for constraining the carbonate chemistry speciation in various settings, including coastal areas, marginal seas, sediment pore waters, hydrothermal fluids, and seawater in the past. Here we present experimentally determined K1* and K2* data for seawater of non-standard major ion compositions based on closed-cell potentiometric titration of artificial seawater that systematically differ in [Mg2+], [Ca2+], [SO42-], and temperature at a fixed ionic strength (0.7 mol/kg-sw). We will present sensitivity analyses of our data and comparisons to existing K1* and K2* data derived through aqueous chemical speciation models. Furthermore, we will discuss implications of our data for carbonate chemistry reconstructions and atmospheric CO2 through time based on changes in major ion seawater composition.