

Bicarbonate-Rich Liquid Condensed Phases in Seawater: Possible Influence on Carbonate Biomineralization

B. CONSTANTZ¹ AND M.A. BEWERNITZ^{2*}

¹Dept. of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305, USA
(brentc@stanford.edu)

²Blue Planet Ltd., Los Gatos, CA 95032, USA
(*correspondence: mark@blueplanet-ltd.com)

Earth's atmosphere has seen extraordinary variation in levels of atmospheric carbon dioxide over Phanerozoic time, although we are currently experiencing a relatively rapid rise in pCO₂ due to the industrial revolution. Modern pCO₂ levels are thought to be relatively low compared to past Era's of prolific carbonate biomineralization during Earth's history when atmospheric carbon dioxide levels were considerably higher, and when most calcium carbonate forming taxa originated and flourished. Recently, it has been observed that the bicarbonate ion, in the presence of calcium and other ions, condenses into a bicarbonate-rich liquid condensed phase (LCP) by fractionating from solution as droplets in the bulk solution. The concentration of the bicarbonate-rich LCP in seawater is affected by atmospheric pCO₂ concentrations and may affect the formation of calcium carbonate mineral phases and basic biomineralization processes. The bicarbonate-rich LCP droplets are about 100 nm across and appear to participate in fundamental biomineralization processes during the formation of calcium carbonate skeletons. We have detected this phase in modern seawater and in artificial solutions mimicking ancient seawater using Nanoparticle Tracking Analysis (a light scattering technique) and other analytical techniques, and found it to be ubiquitous. Discovery of a this co-existent second liquid phase in seawater calls into question the interpretation of seawater analytical measurements, such as pH and concentration estimates of dissolved inorganic carbon taken from filtered seawater, made with the assumption that seawater is a one-phase system. The presence of the bicarbonate-rich LCP in modern seawater suggests that bulk concentrations of dissolved inorganic carbon in seawater may be considerably different than estimated. In addition, some of the previous assumptions about the effect of the pH of the bulk solution phase on biomineralization, in light of the LCP discovery, may miss the role the bicarbonate-rich LCP plays in carbonate biomineralization, and may require further evaluation.