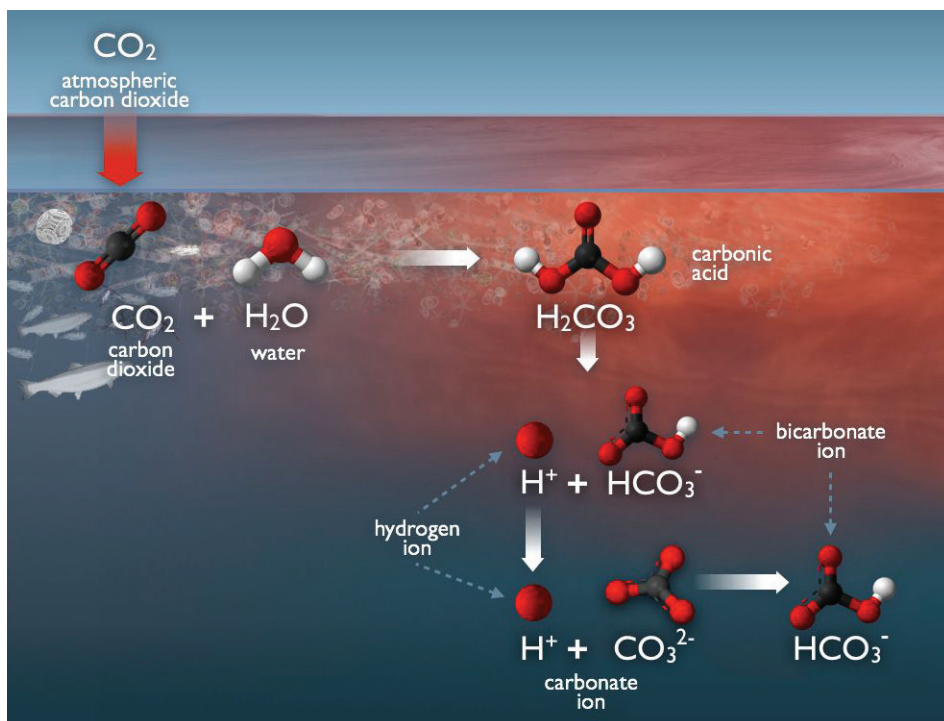


APXPS Finds Carbonate Reversal at Liquid Interfaces



A prime example of carbonate chemistry at an (air/water) interface: the ocean surface. The ocean is the largest sink for the greenhouse gas, carbon dioxide (CO₂). Atmospheric carbon dioxide combines with water to form carbonic acid (H₂CO₃), which then forms carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) ions. From there, carbonate ions can react with dissolved calcium or magnesium ions to form limestone or other minerals, where carbon can become sequestered. Image created by the Center for Environmental Visualization at the University of Washington; reproduced here courtesy of the NOAA Pacific Marine Environmental Laboratory (PMEL) Carbon Program (<http://www.pmel.noaa.gov/co2/>).

Dissolving carbon dioxide (CO₂) in water produces carbonate systems that are key to many processes essential to life, from the buffer system that regulates pH levels in blood, to the carbon cycle that governs CO₂ uptake by Earth's oceans. A detailed understanding of such systems is complicated by the presence of an interface—a cell membrane or the ocean surface, for example—that the CO₂ must cross and that could affect the behavior of the various carbonate species (molecules containing the carbonate ion, CO₃²⁻). At the ALS, researchers have used

ambient-pressure x-ray photoemission spectroscopy (APXPS) to probe the relative concentrations of carbonates near an interface, finding a surprising reversal in the expected abundances of carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) as a function of depth. The results raise important questions about what is really happening at interfacial regions, with relevance to topics ranging from carbon sequestration to biomedical research.

Earlier studies of carbonate systems had used x-ray absorption spectroscopy (XAS) at the ALS to probe the

As We Live and Breathe

Carbonates are commonplace in modern life and are found in everyday items such as baked goods, fizzy drinks, antacids, toothpaste, and cleaners—not a very exotic list of materials! Still, these are all products that rely on certain chemical reactions, such as the generation/neutralization of acid or the uptake/release of CO₂. It turns out that carbonate chemistry is interesting to scientists because carbonate reactions play a major role in mechanisms that cycle CO₂, not just through respiration in our bodies but through our planet's biosphere as well. Carbonate systems help maintain healthy pH levels in the bloodstream while waste CO₂ (produced by cell metabolism) is transported to the lungs to be exhaled. Oceanic carbonate chemistry governs CO₂ uptake by surface waters, with implications for ocean acidification, biomineralization in marine organisms, carbon sequestration, and climate. In this work, Lam et al. report an unexpected result that should stimulate further theoretical discussion of some very intricate chemistry with profound practical implications.

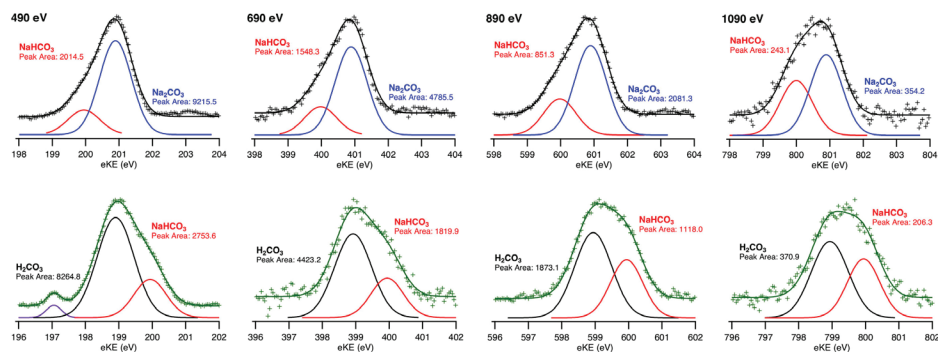
arrangement (hydration structure) of carbonate species and CO₂ in water. The results showed how CO₂ molecules dissolve in water to initiate the production of carbonic acid (H₂CO₃) and bicarbonate ions (HCO₃⁻). However, XAS is mainly a bulk-sensitive technique. To gain access to important details occurring at interfaces, the researchers turned to APXPS, a surface-sensitive technique that

allows atom-specific characterization of chemical states as well as depth profiling of the overall system. Because electrons emitted with higher energies have greater escape depths (effective attenuation lengths), they provide information about species deeper into the solution than electrons with lower energies. Thus, increases in the incident photon energy correlate to increases in the probe depth.

ALS Beamline 11.0.2 is one of the few beamlines in the world capable of this type of experiment on liquids at near-ambient pressures. Because APXPS involves the detection of electrons, any window used to separate the liquid sample from the detector would block electrons from reaching the detector. Instead, the researchers used a liquid microjet system that they developed, allowing them to directly inject a controlled stream of liquid into the chamber without breaking the vacuum.

A number of aqueous carbonate solutions were probed this way, including a 50:50 mixture of sodium carbonate (Na_2CO_3) with sodium bicarbonate (NaHCO_3), and a 50:50 mixture of carbonic acid (H_2CO_3) with sodium bicarbonate (NaHCO_3). In water, the sodium compounds dissolve into sodium (Na^+), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-) ions. Carbon 1s spectra of the carbonate species were collected using four incident-photon energies, roughly corresponding to depths of 2.0, 3.0, 4.5, and 6.0 nm. Gaussian fits to the data were used to deconvolute the contributions of the various carbonate species. Comparison of the resulting peak areas gave the relative concentrations of each species.

Analysis of the data showed that, as depth increases, the peak-area ratios approach unity, as would be expected in bulk regions of 50:50 mixtures. At shallower depths, however, both carbonic acid (H_2CO_3) and carbonate (CO_3^{2-}) have higher concentrations than bicarbonate (HCO_3^-). This is not surprising for neutral H_2CO_3 relative to charged ions (because electrostatic effects tend to repel ions from interfaces). On the other hand, the



APXPS data collected from 50:50 mixtures of Na_2CO_3 : NaHCO_3 (top, black crosses) and H_2CO_3 : NaHCO_3 (bottom, green crosses) at four different incident-photon energies (490, 690, 890, and 1090 eV), corresponding to increasing depths (roughly 2.0, 3.0, 4.5, and 6.0 nm, respectively). Curves for the individual carbon species are shown in red (NaHCO_3 , top and bottom), blue (Na_2CO_3 , top), and black (H_2CO_3 , bottom).

enhancement of CO_3^{2-} (doubly charged and strongly hydrated—i.e., attracting many water molecules) over HCO_3^- (singly charged and less strongly hydrated) is surprising and appears to conflict with recent models for interfacial ion adsorption.

The researchers suggest that the conflict could be resolved if CO_3^{2-} adsorbs to the interface as an ion pair with sodium (i.e., $\text{Na}^+:\text{CO}_3^{2-}$), neutralizing some of the charge effects mentioned earlier. Further theoretical modeling will be needed to gain greater insight into this unexpected reversal in the depth profile of interfacial carbonate systems.



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