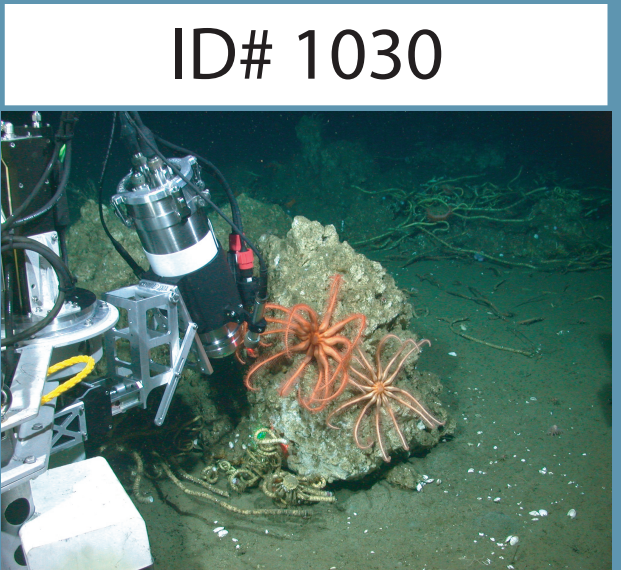




In Situ Ocean Acidification Environmental Observations: MBARI's Cabled Observatory Technology for Controlled Studies of Changing Ocean pH



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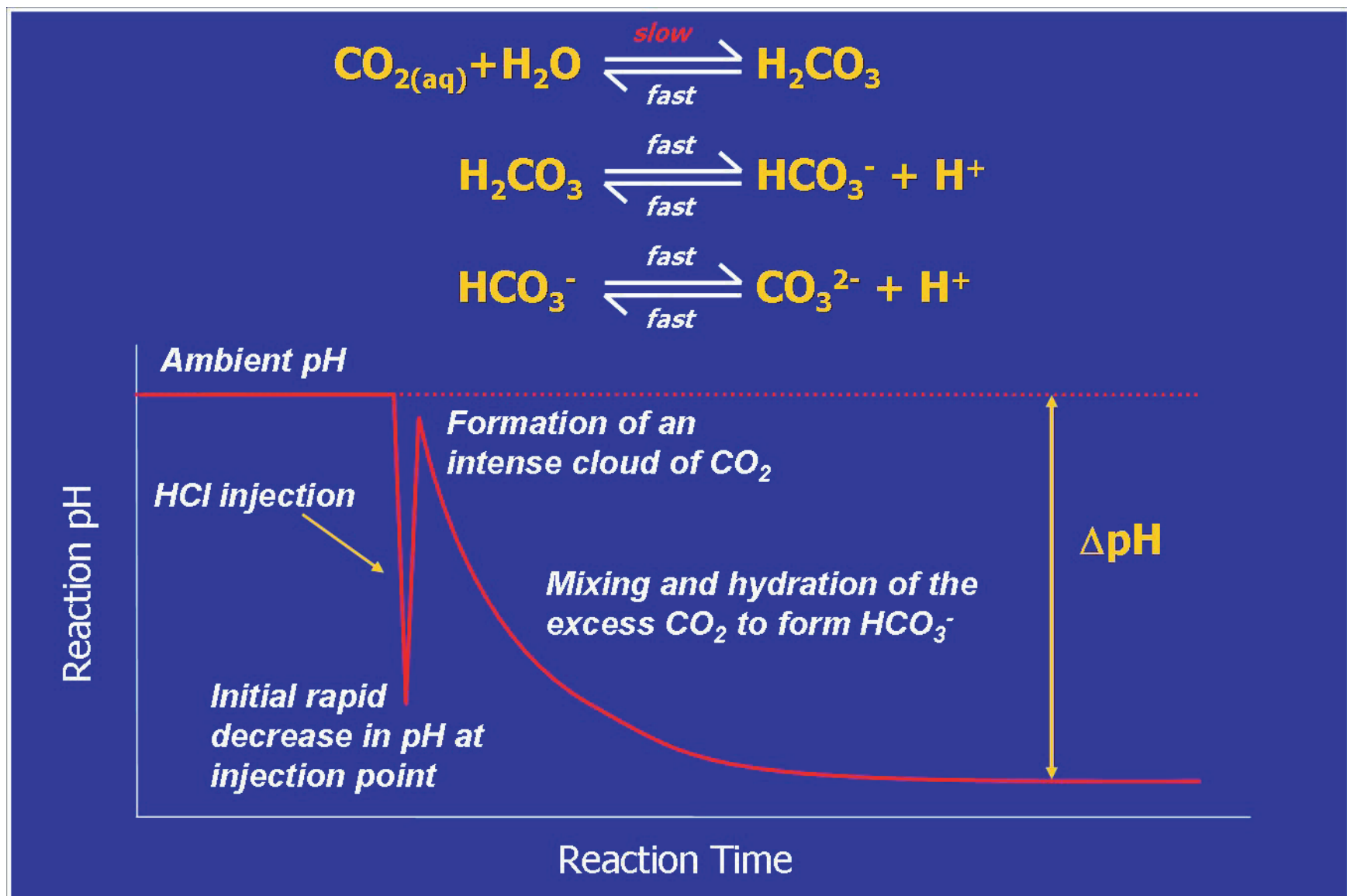
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Abstract - This poster explores modifications to the design, fabrication and implementation of the field tested prototype Free Ocean CO₂ Enrichment (FOCE) system. The proof of concept prototype system was able in the field to control pH perturbations from acid release simulating CO₂ induced pH changes in specific habitat experiments. The acidified flow was pumped so as to maintain a constant delta pH under varying environmental conditions. The modified FOCE system concept is to be powered and supplied by a cable and pipe system from shore, and to move towards CO₂-rich water rather than acid releases. Discussion of the FOCE test results to date indicates paths to improved performance, with a primary problem being system design to accommodate the slow kinetics of the CO₂ hydration reaction in sea water. This paper discloses current MBARI science and engineering efforts and concepts towards an ocean observing system solution by integrating the chemical kinematics of the CO₂-water reaction and the next step in FOCE development for in situ science.

pH Material Options

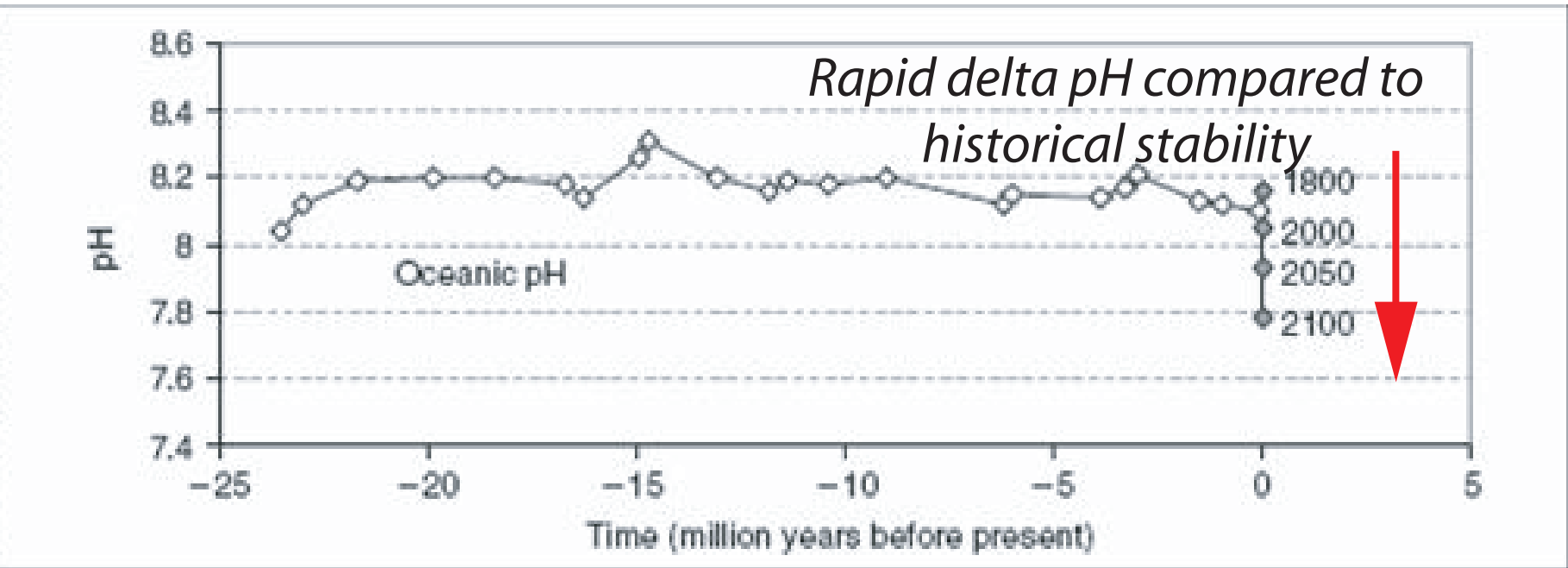


Actively adapting the pH of open ocean water and maintaining a selected value can be accomplished a number of ways. Ultimately each develops a CO₂ concentration which uses the available carbonate to buffer the carbonic acid and restore equilibrium. Hydration of the CO₂ sets the time required for control purposes.

Motivation for Ocean pH Observations

The evolving chemistry of surface sea water under "Business as Usual"

Time	pCO ₂	Total CO ₂	pH	HCO ₃ ⁻	CO ₃ ²⁻	H ₂ CO ₃
yr.	µatm	µmol kg ⁻¹		µmol kg ⁻¹	µmol kg ⁻¹	µmol kg ⁻¹
1800	280	2017	8.191	1789	217	10.5
1996	360	2067	8.101	1869	184	13.5
2020	440	2105	8.028	1928	161	16.5
2040	510	2131	7.972	1968	144	19.1
2060	600	2158	7.911	2008	128	22.5
2080	700	2182	7.851	2043	113	26.2
2100	850	2212	7.775	2083	97	31.8

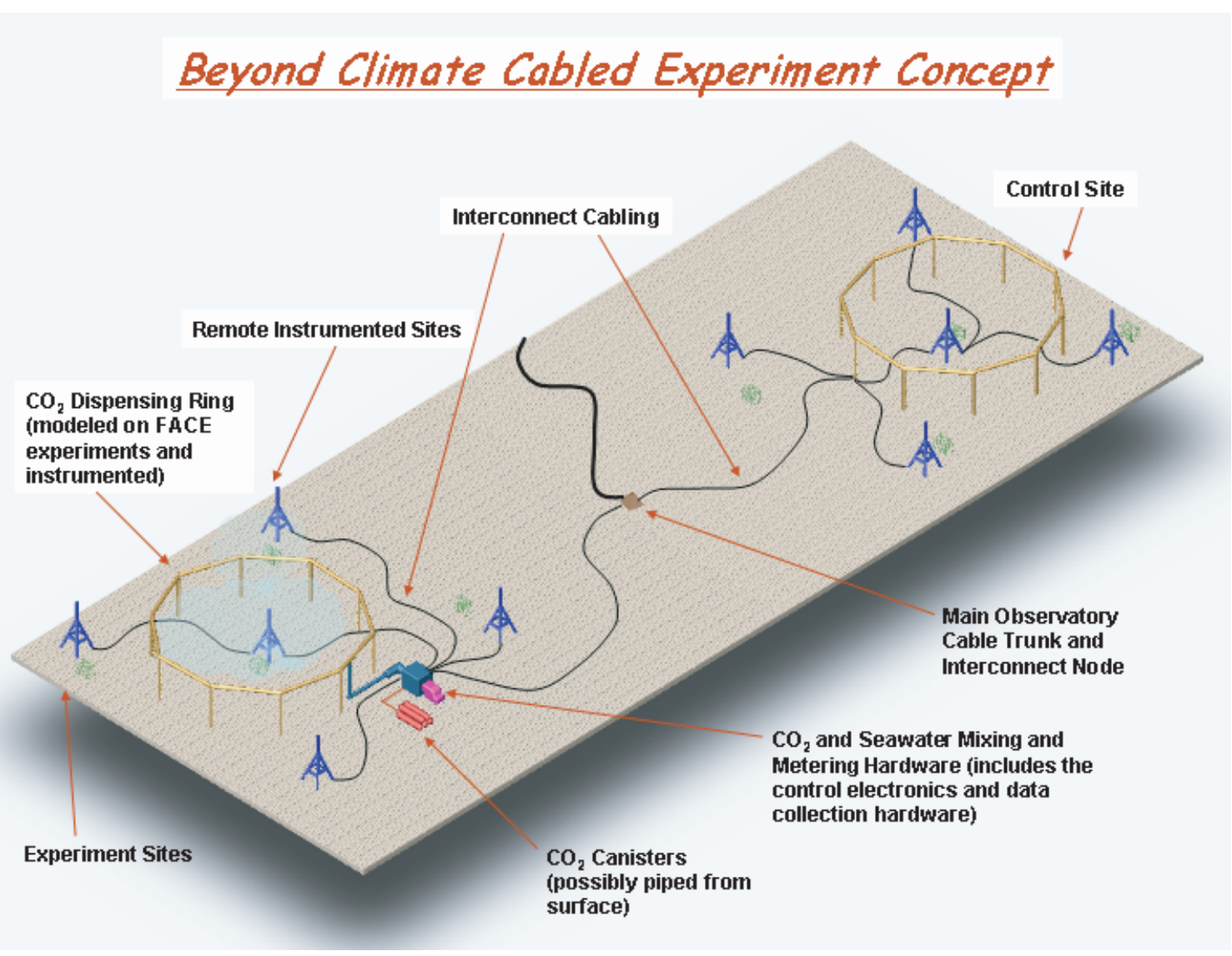


Current predictions estimate that the surface ocean waters will drop in pH from the current level of 8.1 to 7.8 or possibly lower by the end of this century. The need to study the impacts of ocean pH change and consider policy changes and/or action is at hand.

Studying the impact of anthropogenic CO₂ on the atmosphere has been a key aspect of climate change research and the arguments surrounding global warming. Until recently the oceans role in this process has been largely ignored, yet the ocean is the largest buffer absorbing 2 giga-tons of carbon (7 giga-tons of CO₂) per year. What will the future impact be on various habitats of the ocean?

Several elements combined to create the concept of oceanic pH observations.

Free Air CO₂ Enrichment (FACE) experiments began over a decade ago. The FACE experiments had large infrastructure to deliver the necessary CO₂ required to imitate the future world CO₂ ppm.

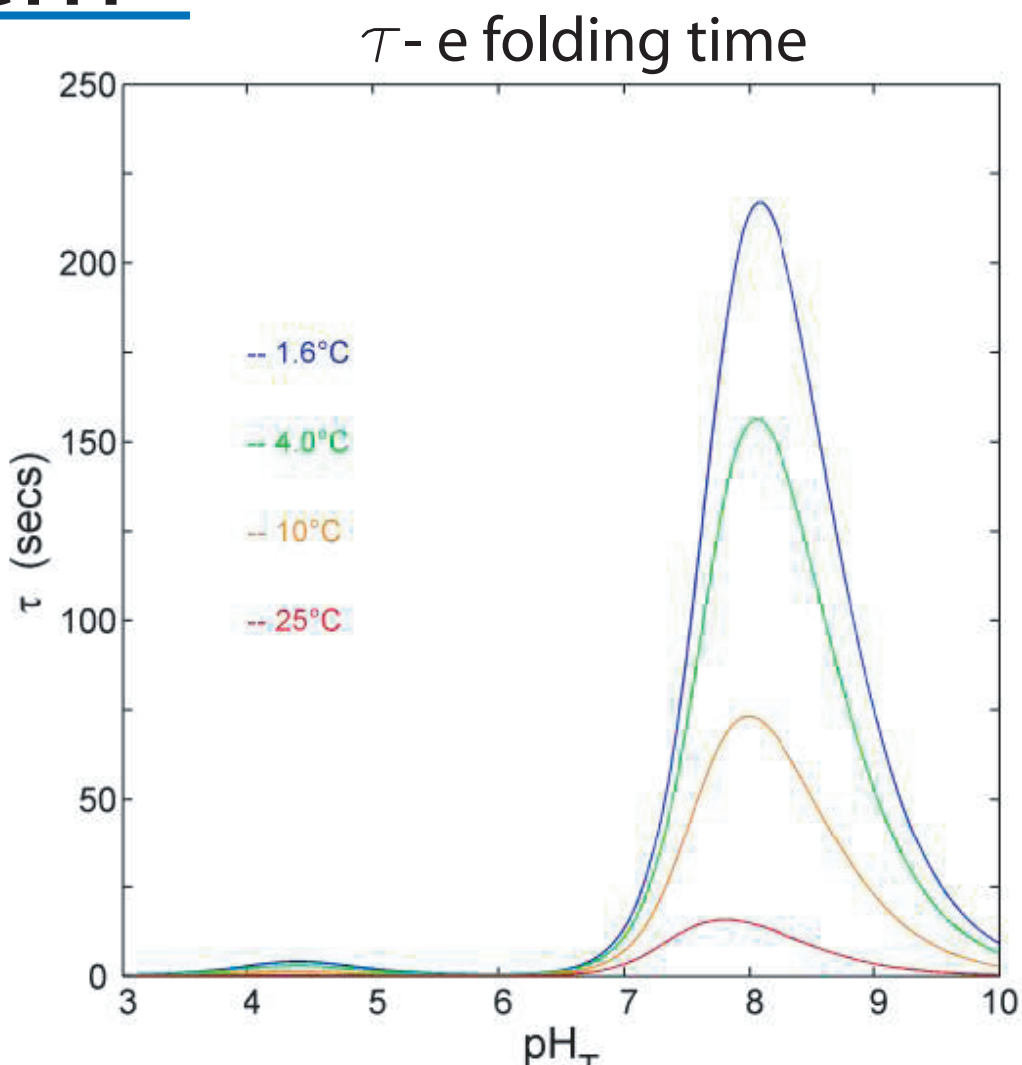
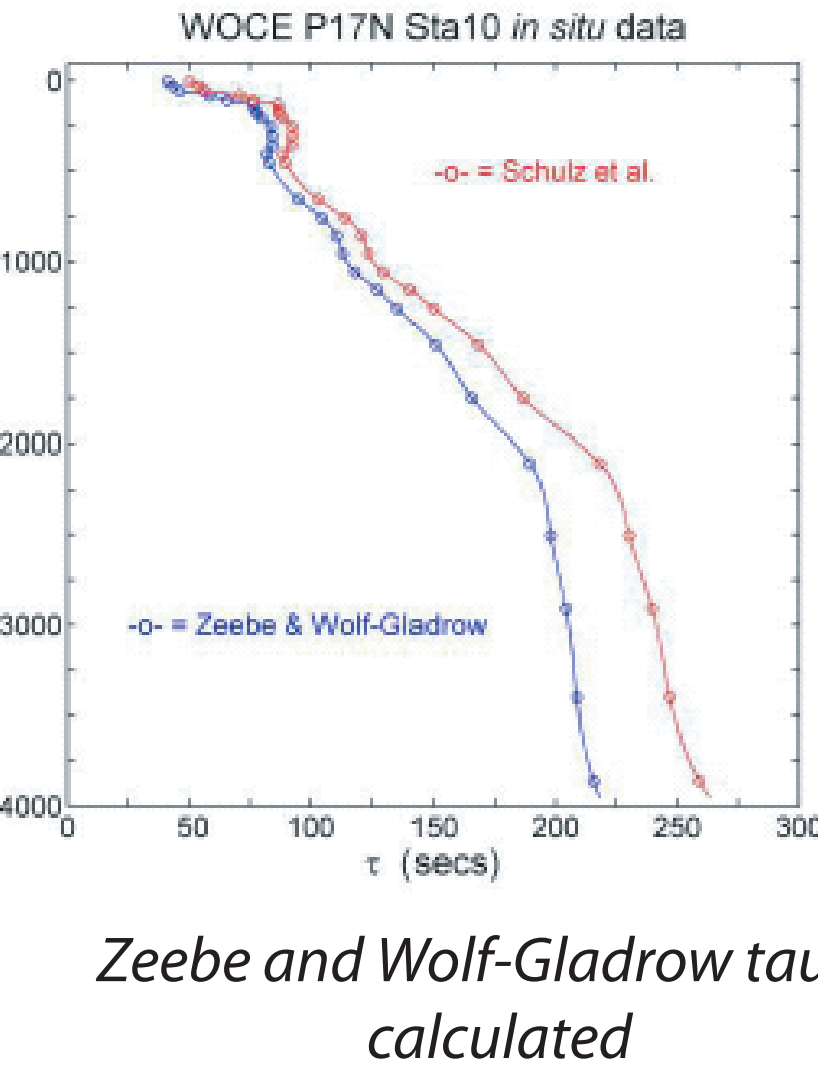


Knowledge Required to Control the System

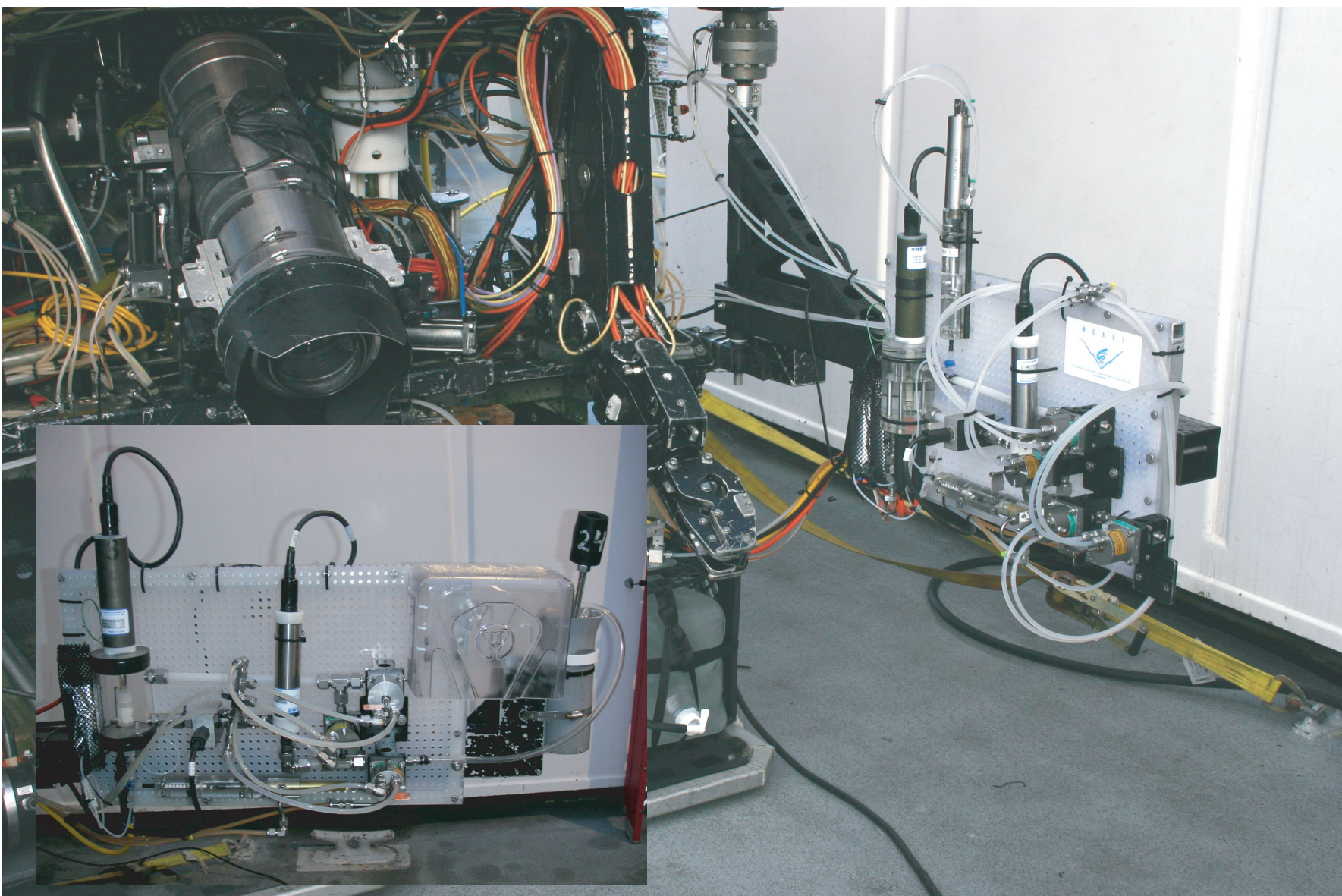
Zeebe and Wolf-Gladrow model equations

$$\begin{aligned} \text{CO}_2 + \text{H}_2\text{O} &\xrightleftharpoons[k_{-2}]{k_2} \text{HCO}_3^- + \text{H}^+ \\ \text{CO}_2 + \text{OH}^- &\xrightleftharpoons[k_{-1}]{k_1} \text{HCO}_3^- \\ \text{CO}_3^{2-} + \text{H}^+ &\xrightleftharpoons[k_{-3}]{k_3} \text{HCO}_3^- \\ \text{H}_2\text{O} &\xrightleftharpoons[k_{-4}]{k_4} \text{H}^+ + \text{OH}^- \end{aligned}$$
$$K_1' = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$$
$$K_w' = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$
$$\frac{1}{r} = +k_{-1} - k_{-1} \left(\partial_b [\text{H}^+] + \partial_h [\text{HCO}_3^-] \right) - k_{-2} \partial_b + k_{-4} \left([\text{OH}^-] + \partial_{oh} [\text{CO}_2] \right)$$
$$\frac{d(\delta \text{CO}_2)}{dt} = -\frac{1}{r} \delta \text{CO}_2$$

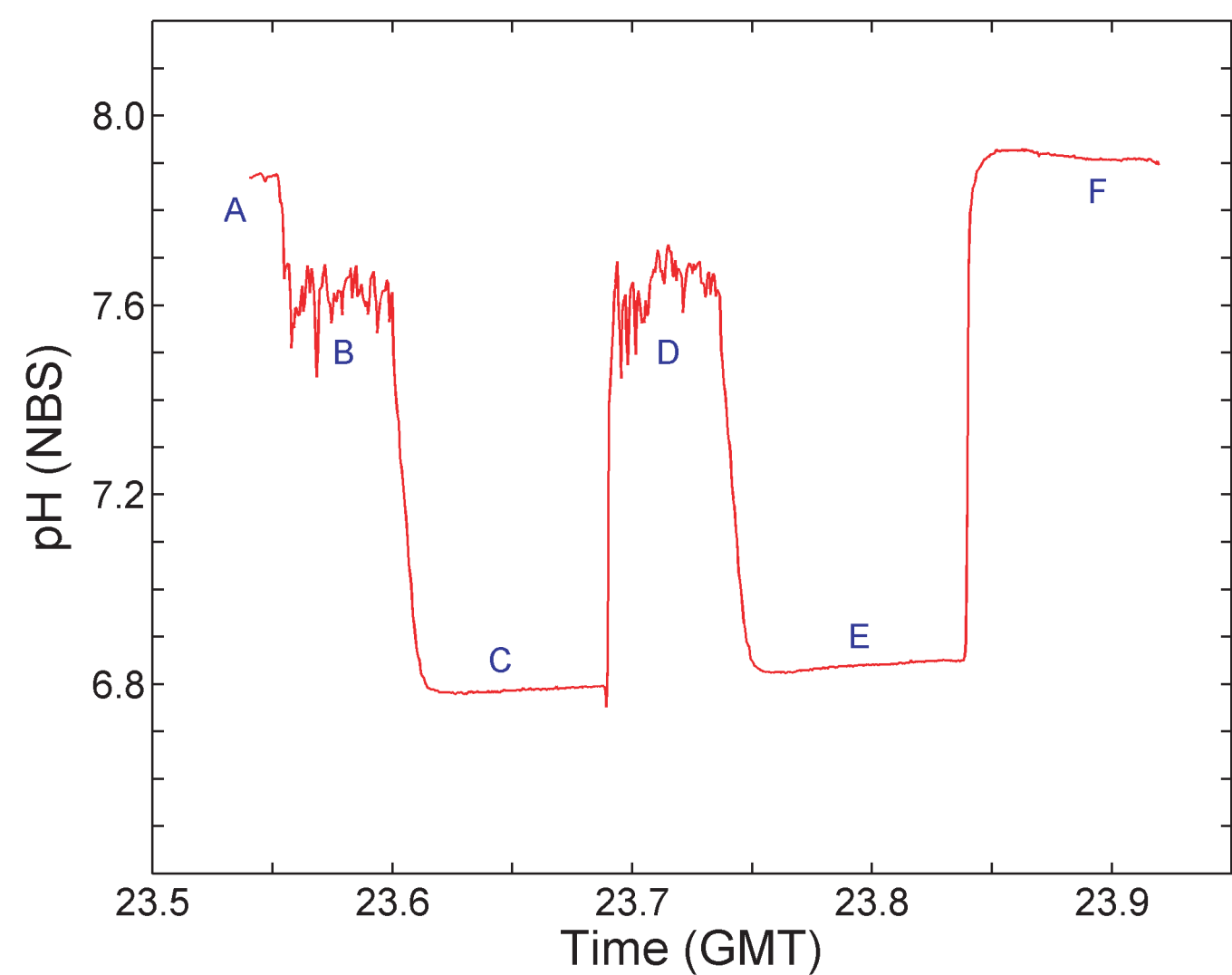
By solving the kinetics problem (T,P) we can predict the time constant to adjust the required CO₂ addition needed to model the desired conditions anywhere. We are able to select residence times based on the e-folding time required to achieve the equilibrium desired. Typically, we strive for 3 e-folding times which is approximately 95% complete, 2 e-folding approaches 88%.



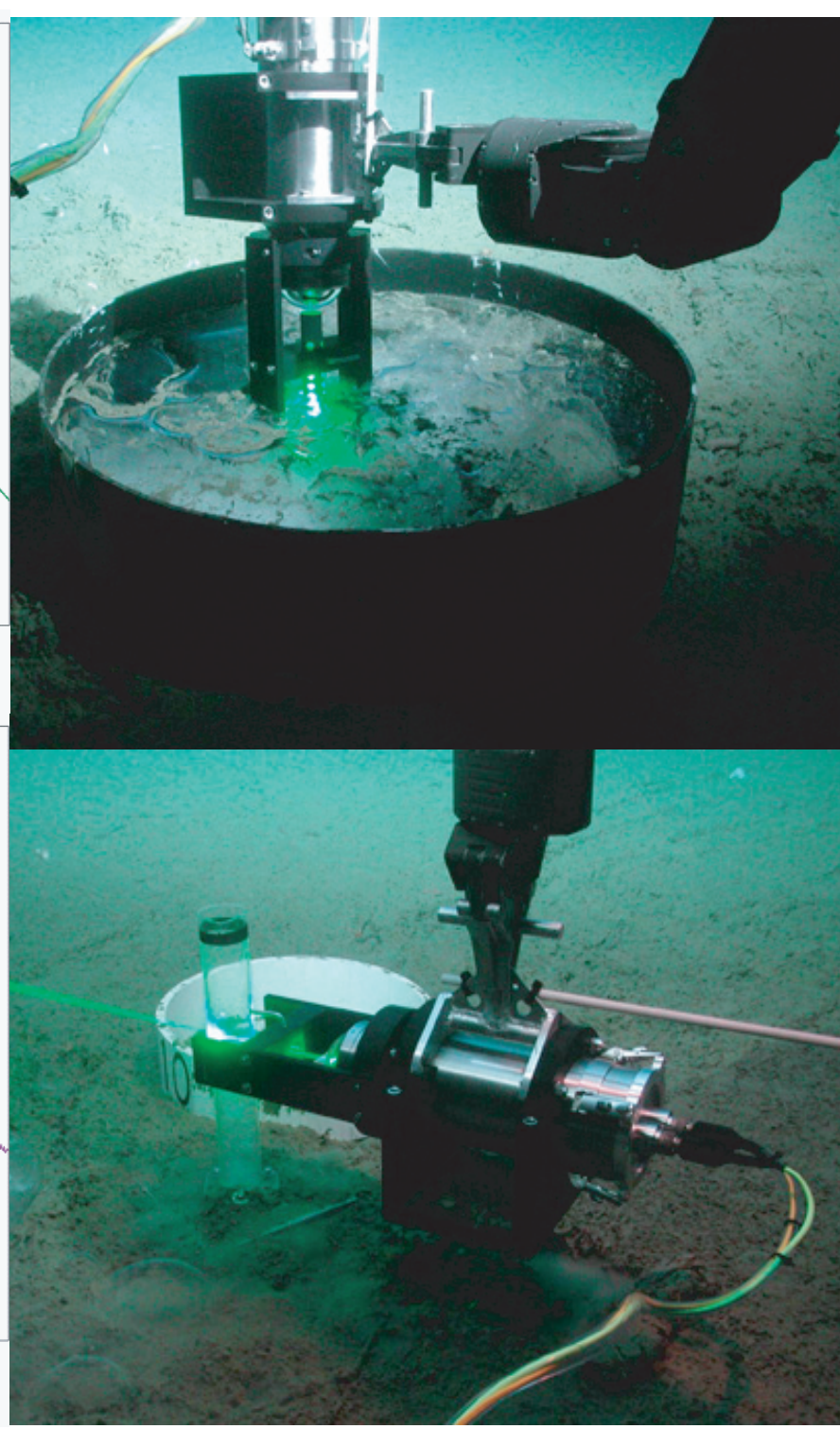
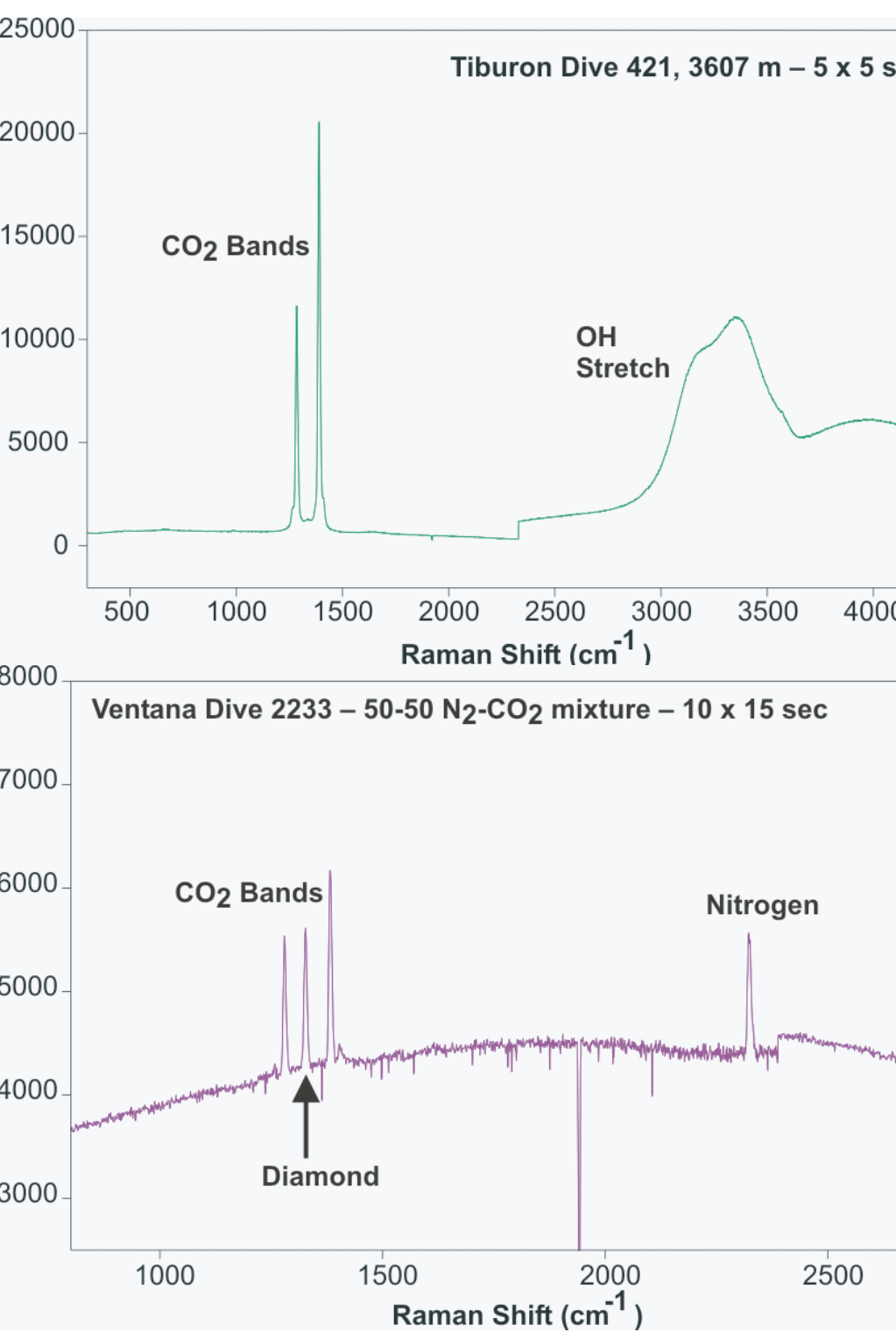
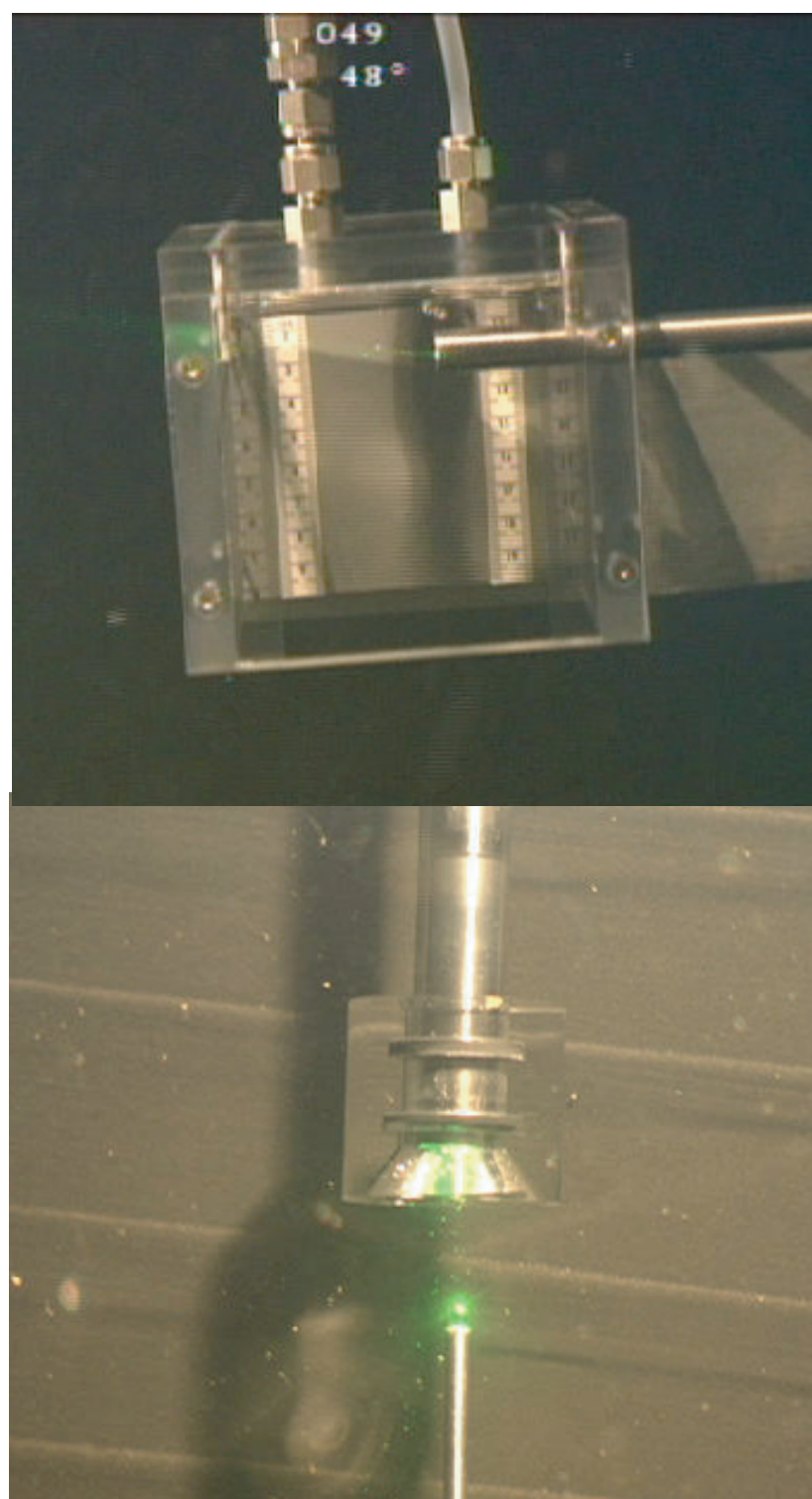
Background Experiments in Support of Ocean pH Observatories



CO₂ sniffer experiments demonstrating the initial pH state, picking up a plume, and showing time to equilibrium

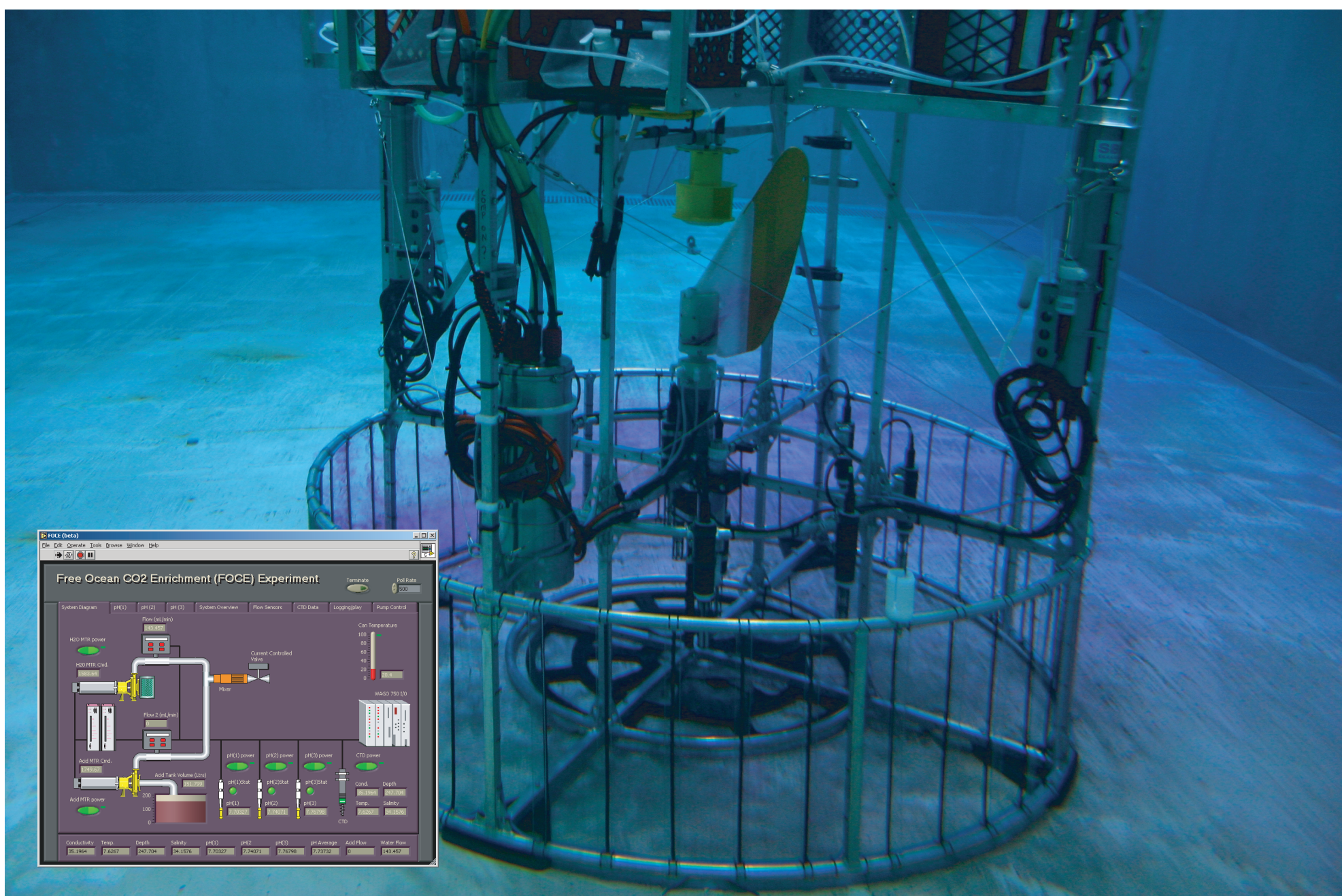


Numerous experiments have been performed to prove theory and demonstrate the underlying in situ kinetics of CO₂. Three such experiments are shown here each contributing a significant element to the CO₂ observatory concept and determining the applicable technologies. The sniffer experiments were performed at various depths with a free plume of CO₂ as released from an open pool (seen in the upper right ring image below). A and F are the background value of pH for the seawater to begin the in situ experiment. B and D are pH values of the sampled CO₂ enriched water collected just above the pool. C and E are the final pH values after equilibrium is reached when the sampled water was pumped in a closed loop. This series of experiments confirmed the Zeebe and Wolf-Gladrow model is the most accurate for the engineering control loop. The multi-injection experiment demonstrated the final pH value not the initial condition determines the e-folding time τ while properly giving consideration to temperature and depth. The laser Raman spectrometer has been used in numerous experiments and has determined the dissolution rate of CO₂ in mixed gas situations while also giving the CO₂ concentration. The calculated CO₂ dissolution in seawater versus Nitrogen (in the graph below) matches the measured values. This is important to us since many applications would require some method of preventing CO₂ hydrate formation and the mixed gas system easily solved the issue.

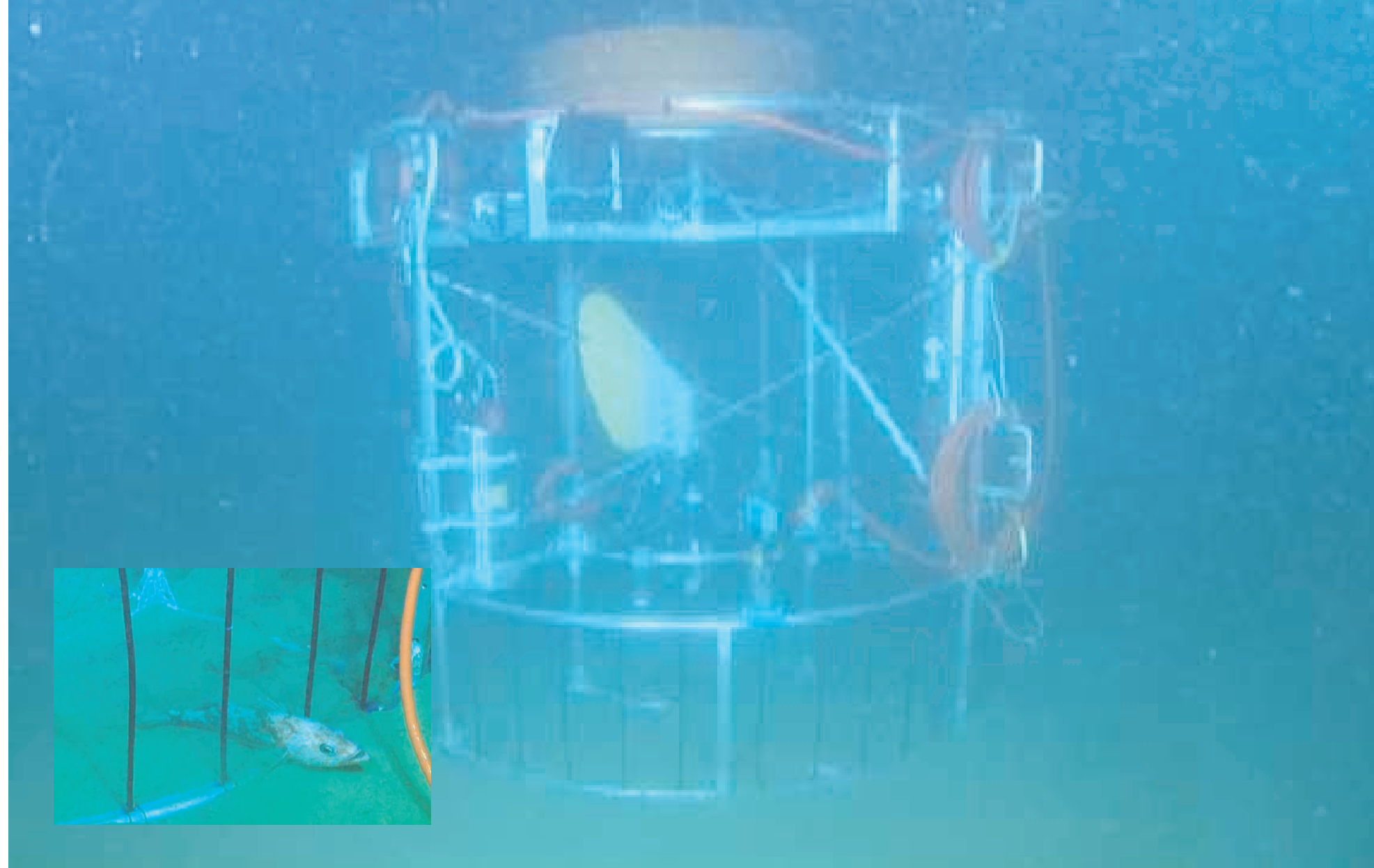


Raman experiments on preferential dissolution of CO₂ in seawater, nitrogen is used to prevent hydrate formation

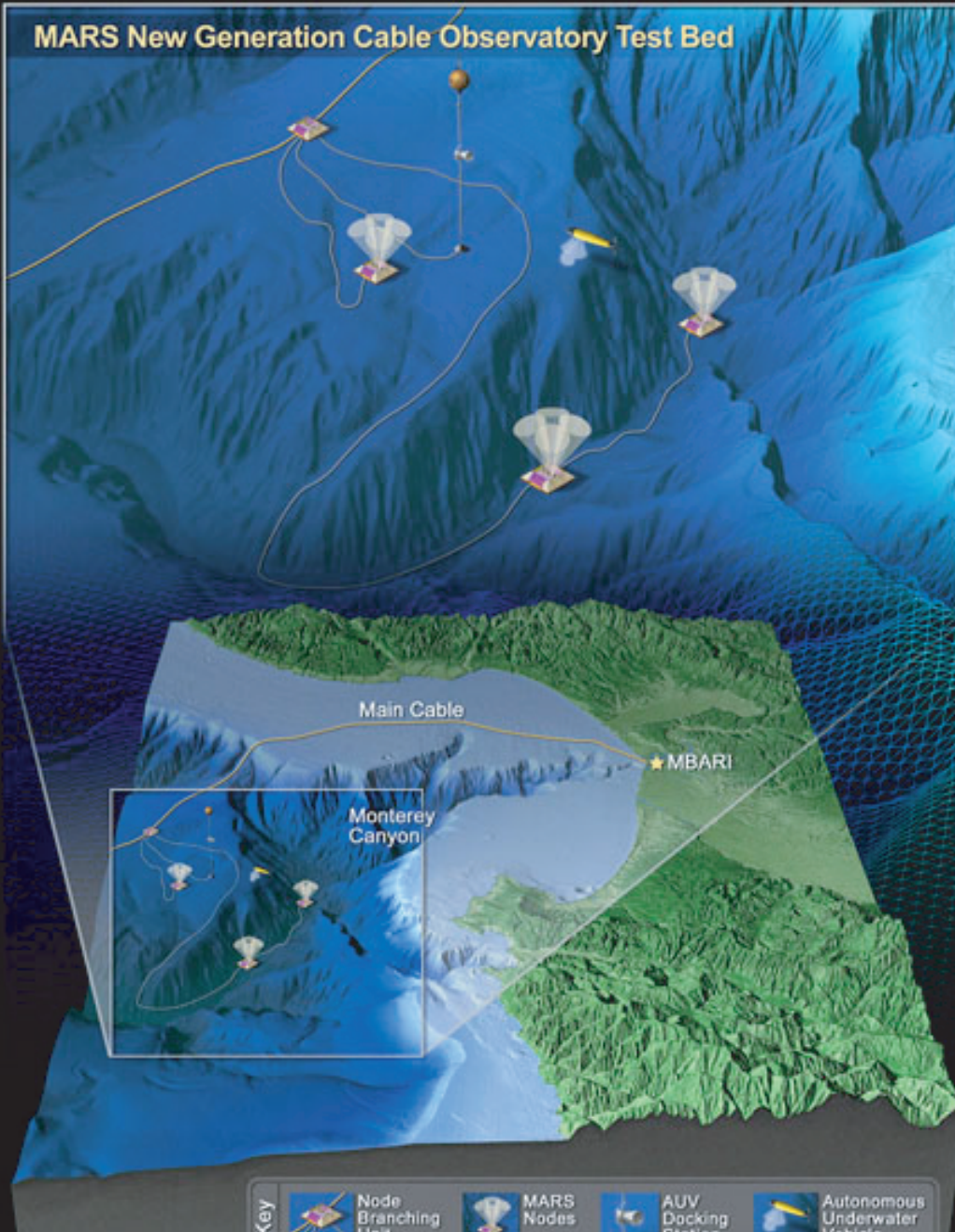
Prototype of an Ocean pH Observatory



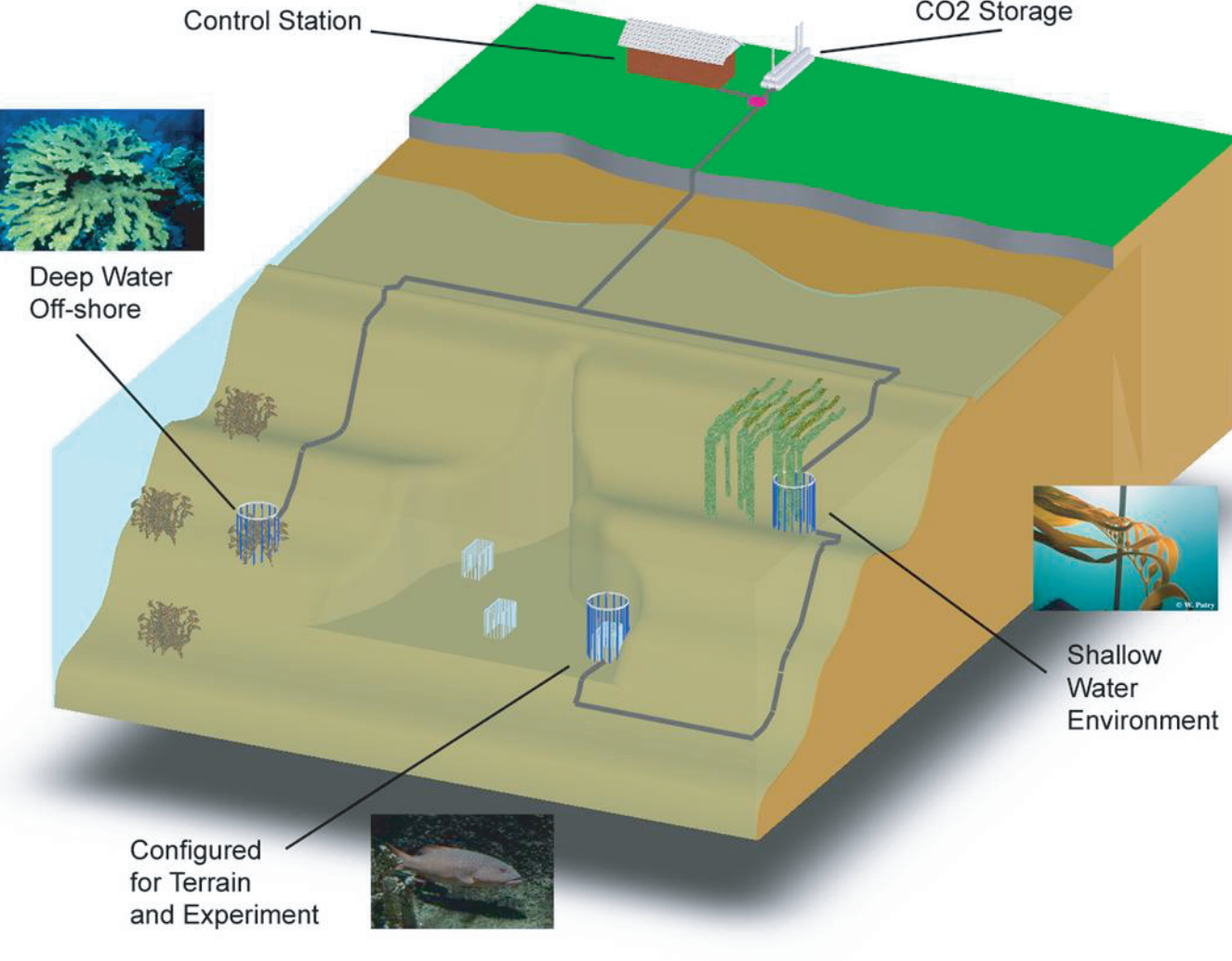
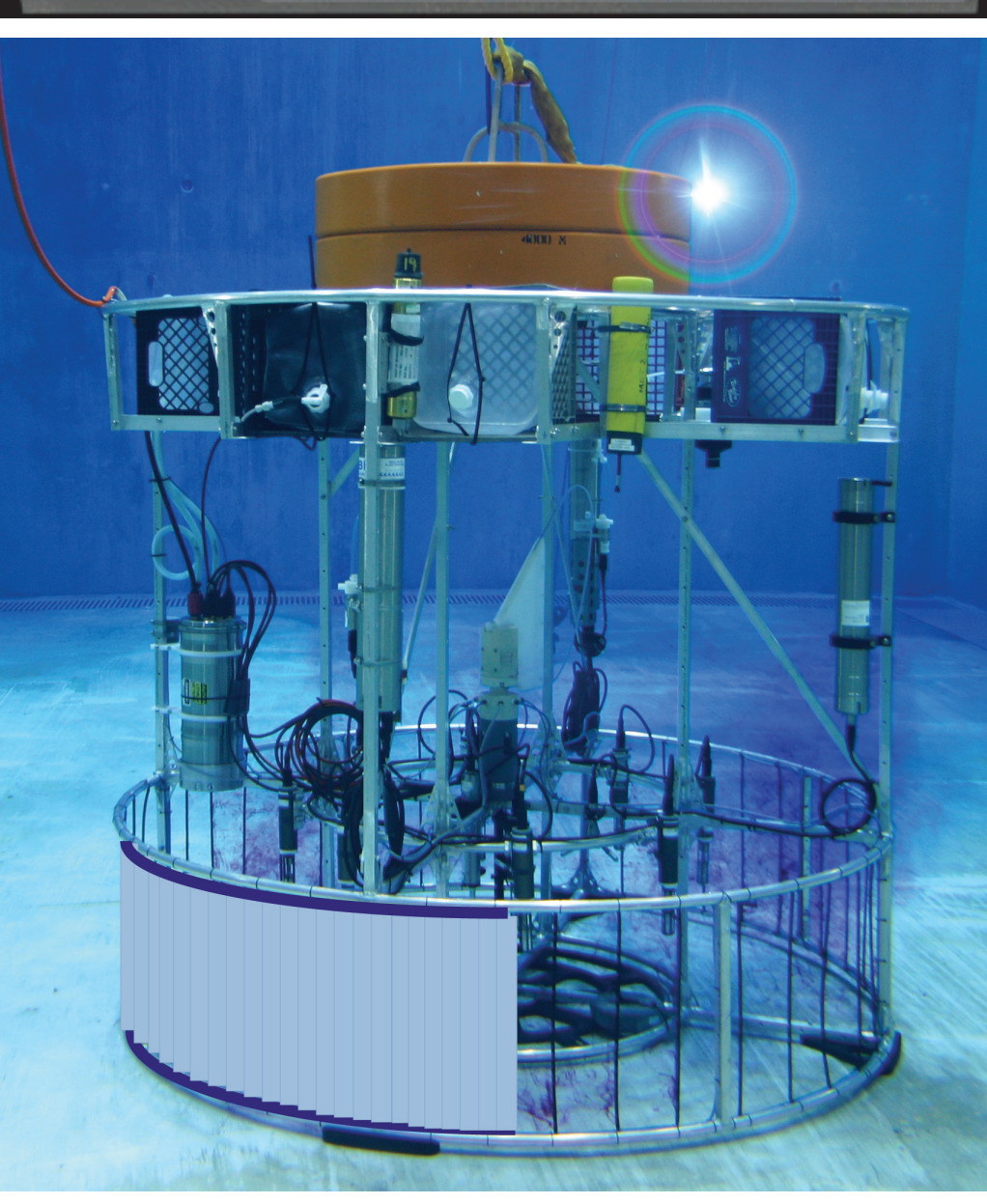
Left is the prototype FOCE frame deployed in the MBARI 10m deep test tank. The flotation pack is on top, cubitainers of concentrated acid are below, the current vane is center, and the control module is at left. The vertical lines on the bottom ring are the emitters. The design is basically comprised of an outer emitter ring, and an inner control volume with the space between the two arranged so as to provide time for mixing and relaxation of the system towards chemical equilibrium. Below is the same device deployed in situ just prior to connecting power and communications. The chart directly below is one result of several tests performed over two days at sea. The graph shows the initial pH of 7.76 in the oxygen minimum zone in the Monterey Bay Canyon. The line below is the offset pH desired and the traces are the several pH probes used to give feedback to the system. The initial input is seen to overshoot here but eventually the system settles down and tracks to the pH commanded.



Ocean pH Observatories - MBARI's Next Step



Testing at MBARI has demonstrated the feasibility of FOCE experimentation for studying enriched CO₂ conditions in the ocean. Several technological hurdles are no longer limiting us and ocean pH observatories are poised to proceed. Remaining questions we are researching at this time involve logistics. The first issue regards CO₂ use and scalability. Several options are available but the desired 3e-folding time is the driver. There are several options to manage resources which would be decided on operational conditions. The more difficult problem is permitting. The science community and governments around the world are proceeding together to build ocean observatories and advancing the technology to study anthropogenic CO₂ impact and other serious and societally relevant questions. We are hopeful as awareness is raised and understanding increased the permitting question will be much easier.



One concept for material is to control flow