Introduction: The DuraFET pH sensor is a key component of global ocean observational networks through coordinated efforts like Biogeochemical (BGC) Argo (Claustre et al. 2020) and the Global Ocean Acidification Observing Network (Newton et al. 2015). It is the only oceanographic pH sensor capable of generating high quality data that also has the demonstrated ability to be deployed in large numbers and routinely operate to depths of 2 km or more over several years with no maintenance. For example, DuraFET pH sensors have been deployed on hundreds of profiling floats (Johnson et al. 2017a; Maurer et al. 2021), dozens of ocean moorings (Hofmann et al. 2011; Martz et al. 2014; Takeshita et al. 2015), numerous gliders (Saba et al. 2019; Takeshita et al. 2021a), and in a variety of ocean environments from the deep-sea, coral reefs (Takeshita et al. 2016; Cyronak et al. 2019), tide pools (Chan et al. 2017), kelp forests (Frieder et al. 2012; Hirsh et al. 2020; Traiger et al. 2021), seagrass beds (Ricart et al. 2021), and more. They have generated unprecedented data sets, such as those in Hofmann et al. (2011) with over 900 citations in Google Scholar. The sensors enable measurements for air-sea carbon dioxide exchange (Gray et al. 2018; Bushinsky et al. 2019a), coral reef productivity (Takeshita et al. 2016, 2018a), biological carbon uptake (Johnson et al. 2022), ocean acidification (Swart et al. 2018; Bronselaer et al. 2020), and a variety of other ecosystem processes. Furthermore, they have been widely used in the laboratory for ocean acidification mesocosm studies (Bockmon et al. 2013; Kapsenberg et al. 2017; Toy et al. 2022) and to study CO_2 thermodynamics (Takeshita et al. 2017). Finally, the DuraFET pH sensor is a vital component of other carbon system sensors such as the solid state Titration Alkalinity sensor (Briggs et al. 2017, 2020). Clearly, this sensor has, and will continue to play an indispensable role in ocean carbon observing from local to global scales.

The core enabling technology of the DuraFET pH sensor is an Ion Sensitive Field Effect Transistor (ISFET) semiconductor device (Bergveld 2003) that is produced by the Honeywell Co. at their facility in Plymouth, MN (Martz et al. 2010). Although there are other ISFET manufacturers, the Honeywell device has a variety of unique features (discussed below) that give it the performance required for ocean applications such as long term stability (Martz et al. 2010) and Nernstian response (Takeshita et al. 2014). These features are lacking in most other competitors. In a surprise statement in June 2022, Honeywell announced that they have ceased production of this semiconductor device due to the modest market size and the retirement of key personnel involved in its production. The end of DuraFET production creates a major hole in the global ocean carbon observing system.

This proposal is a response to address this imminent and urgent problem that is reverberating across the oceanographic community. *The main objective for this project is to accelerate the development of an alternative pH sensor that can be scaled to fit the current needs of global ocean observational networks.* While there are other, high quality commercially available pH sensors such as those based on spectrophotometry (e.g., SAMI pH (Seidel et al. 2008; Lai et al. 2018) or the Clearwater pH sensor (Monk et al. 2021)), these sensors are complicated due to the need for pumps and valves, and have not demonstrated the robustness and reliability that is required to scale globally on a variety of autonomous platforms that have stringent power, size, and weight requirements such as floats and gliders. Here, we propose to explore two promising technologies: 1) assess the performance of an optical pH sensor (Pico-pH) by PyroScience; and 2) develop a pH sensor that utilizes an ISFET from another supplier. Sensor performance will be thoroughly characterized in the laboratory and in the field through deployments on moored coastal environments, underwater gliders, and profiling floats. Results from this development will be rapidly and efficiently shared with the oceanographic community through recurring webinars, publications, and collaboration with industry.

Background

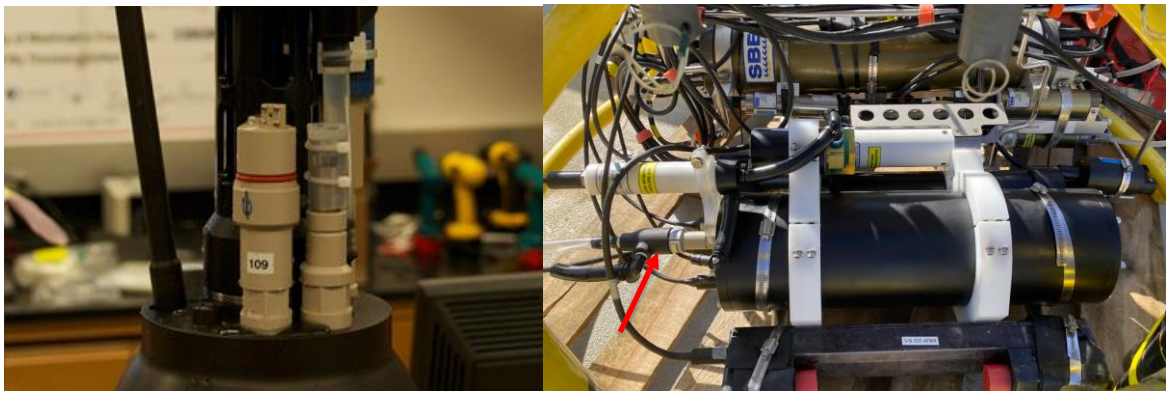


Figure 1: (left) A DSD pH sensor (labeled 109) installed onto an APEX profiling float head, and (right) a SeapHOx sensor with arrow pointed at DSD.

DuraFET pH sensors are mainly utilized by the community through autonomous data loggers for moored systems (e.g. SeaFET and SeapHOx; (Bresnahan et al. 2014)), in mesocosms to manipulate and monitor pH levels (Kapsenberg et al. 2017), and Deep-Sea-DuraFETs (DSD) for profiling applications such as floats and gliders (Johnson et al. 2016; Takeshita et al. 2021a). pH can be measured using an internal reference for the Honeywell DuraFET combination electrode (SeaFET, SeapHOx, and mesocosms), or by using an external reference electrode (chloride ion selective electrode; Cl-ISE) that is exposed directly to solution. Details for the calculations can be found in Martz et al. 2010 and Johnson et al. 2016, but will be summarized below for the external reference with a focus for the DSD.

The DSD is a potentiometric pH sensor (Figure 2) that consists of a Honeywell ISFET and a Cl-ISE as the reference electrode that is exposed directly to seawater and housed in a pressure tolerant package (Johnson et al. 2016). This solid state sensor has demonstrated excellent stability and performance in seawater (Martz et al. 2010), and is a proven technology capable of autonomous deployments for years (Johnson et al. 2017a; Maurer et al. 2021). The ISFET responds to H^+ activity in solution, whereas the Cl-ISE responds to Cl^- activity. Thus, in essence, the DSD is measuring the activity of HCl in seawater, which can be converted to the free $[H^+]$, or pH on the free scale (pH_F), using published HCl activity coefficients (Khoo et al. 1977) and $[Cl^-]$ calculated from salinity (Dickson et al. 2007). Therefore the sensor signal Vrs, or the voltage between reference electrode and the source of the ISFET, can be expressed as:

$$Vrs = k_{T,P} - RT_K \ln(10)/F \times \log(a_{H+}) - RT_K \ln(10)/F \times \log(a_{Cl-})$$

$$= k_{T,P} - RT_K \ln(10)/F \times \log(\gamma_{\pm HCl}(T,P)^2) - RT_K \ln(10)/F \times \log(m_{H+}) - RT_K \ln(10)/F \times \log(m_{Cl-})$$

where R is the universal gas constant, T_K is temperature (T) in Kelvin, F is the Faraday constant, a and m represents the activity and molality for the respective ions, and $\gamma_{\pm HCl}$ represents the mean activity coefficient of HCl at in situ T and P. The reference potential ($k_{T,P}$) is the sensor specific calibration function, and can be calculated when Vrs is measured in a solution with known a_{HCl} over a range of T and P, and consists of three terms:

$$k_{T,P} = k_0 + k_2 \times T_C + f(P)$$

where $k_{T,P}$ is the reference potential at in situ T and P, k_0 is the constant term ($k_{T,P}$ at 0 °C and 1 atm), k_2 is the temperature coefficient, T_C is temperature in Celsius, and $f(P)$ is the pressure term fitted to a polynomial

in P. k_2 and f(P) are determined for each DSD in a 0.01 M HCl solution in the laboratory, as a_{HCl} is well characterized over large ranges in T and P (Harned and Ehlers 1933; Harned and Owen 1963). The DSD is T and P cycled inside a custom built titanium pressure chamber. P is cycled from 0-2000 dBar while maintaining a constant temperature, and is repeated at temperatures between 2 – 20 °C. Once $k_{T,P}$ is quantified, pH_F can be calculated by:

$$pH_F = -\log_{10}(m_{H+}) = (Vrs - k_{T,P}) \times F/(RT_K \ln(10)) + \log_{10}(m_{Cl-}) + \log_{10}(\gamma_{\pm HCl}(T,P)^2)$$

Finally, a conversion to pH on the total scale (pH_T) is made by:

$$[H+]_T = [H+]_F \times (1 + S_T/K_S)$$

where S_T is the total sulfate concentration calculated from salinity, and K_S is the dissociation constant for HSO_4^- at in situ conditions (Dickson 1990).

The DSD is a core sensor in the Biogeochemical-Argo suite of sensors (Claustre et al. 2020). More than 200 of these sensors have been deployed on profiling floats in the SOCCOM (Southern Ocean Carbon and Climate Observations and Modeling) project, and the GO-BGC (Global Ocean Biogeochemistry Array) infrastructure project. Over the next 3 years, an additional 400 profiling floats with pH sensors are scheduled to be deployed between these two programs. In addition, dozens of DuraFET pH sensors have been deployed by other nations as part of the international Argo program. Details on sensor performance are outlined in Johnson et al. (2017) and Maurer et al. (2021). On average, the DSD drifts by -0.002 ± 0.032 per year across the Argo array, but these drifts are correctable using procedures outlined in Johnson et al. (2017) and Maurer et al. (2021). As a result of these quality control methods that have been developed, DSD pH values show agreement with discrete samples to 0.002 ± 0.015 (n = 1145), demonstrating excellent performance in the field. Additionally, recent refinements of the DSD suggests reduced drift rates. For example, a new implementation of the DSD, termed the Gasket DuraFET (GDF) shows reduced sensor drift, and the handful of GDFs that have been deployed on floats shown no significant drift on profiling floats over years. The use of a gasket to create the mechanical seal for the sensor should lead to superior reliability as well.

The GO-BGC and SOCCOM projects have acquired a sufficient stock of ISFET semiconductors to sustain both programs for several more years. The GDF design will be used for these future sensor builds. After the stock of Honeywell ISFET chips is exhausted, no pH sensor deployments by these programs will be possible without new sensor development. The commercial supplier of these sensors (Sea-Bird Scientific, SBS) has even fewer sensors in stock and is already declining to refurbish mooring instruments from their prior customers and is only taking a limited number of orders for sensors on profiling floats. In fact, Seabird and our team were told about the decision to discontinue the ISFET in June 2022, but in fact the decision was made internally at Honeywell approximately a year before that. This is leading to long lead times for any DuraFET sensors distributed by Honeywell, and they anticipate many orders will not be fulfilled. Therefore the community is already experiencing a shortage of DuraFET pH sensors.

The impact of the discontinuation of the DuraFET has far reaching impacts beyond the profiling float programs as well. NOAA is compiling information about how this would impact NOAA-funded activities. Preliminary results from this survey suggest that “the overwhelming response is that NOAA’s mission to monitor and detect changes in the ocean will be *severely impacted within the next year*, specifically for coral reef management, effects of ocean acidification on marine fishes, total ocean carbon budget, delayed implementation of Biogeochemical Argo, and understanding of ecosystem responses to

climate (i.e. California Current)" (personal communication, E. Smith). NOAA purchases approximately 300 DuraFETs each year to support their monitoring efforts, and all of these programs will be affected on the timescale of months to a year as DuraFET sensors fail and cannot be refurbished. Impacts on programs outside of NOAA have not been quantified, but all will be impacted on similar timescales. Clearly, we need an alternative solution as soon as possible.

Finally, we note that because of NOAA's critical need for DSD pH sensors they are working with multiple federal agencies in an effort to influence Honeywell to restart production. The outcome of that effort remains unknown. However, the critical need for robust pH sensors in ocean science mandates that we follow the paths outlined in this proposal so that the community has robust alternatives for pH measurements, rather than relying on a sole-source supply. Further, there is some likelihood that the improved ISFET option discussed below could result in superior reliability, when compared to the Honeywell chip due to a larger mechanical size.

Research approach and preliminary data

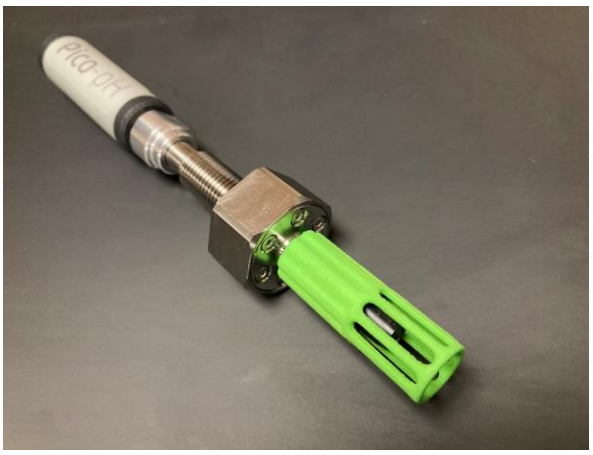


Figure 2: Photo of the pH optode Pico-pH sensor

We propose to test and develop two promising pH sensor candidates that are capable of long-term deployments (years) to 2 km depth on autonomous platforms such as profiling floats and gliders, as well as for moored instrumentation and laboratory mesocosm applications. First, we will test and characterize a commercially available optical pH optode sensor (Staudinger et al. 2018, 2019) distributed by PyroScience. This is a relatively new sensor for oceanography, thus its performance has not been thoroughly characterized to the satisfaction of chemical oceanographers. Its preliminary characterization looks promising. Second, we will develop a pH sensor similar to the Deep-Sea-DuraFET but using an ISFET from a different supplier. There are several key characteristics for the Honeywell ISFET that enable high quality performance, and we believe we have identified a supplier that meets our requirements. Both pH sensors that will be explored here are solid state, small, and low-powered, making them good candidates for autonomous platforms. We will thoroughly characterize both sensors for pH response (practical vs. ideal/theoretical), long term drift (months to years), salinity, temperature, and pressure effects, response time, and hysteresis. Finally, we will deploy both sensors on coastal moorings, underwater gliders, and profiling floats to assess in situ performance across a range of conditions over months to years.

pH Optode: Optical optode chemical sensors have found widespread success in oceanography, mainly for measuring O_2 (Tengberg et al. 2006; Johnson et al. 2015; Bittig et al. 2018a). These sensors have the benefit of being small, solid state, low power, and robust. Additionally, O_2 optodes exhibit very low drift once deployed (typically <1% per year; (Bushinsky et al. 2016; Maurer et al. 2021)), making them ideal for long term autonomous applications. As a result, they are the standard O_2 sensors for BGC-Argo floats (Bittig et al. 2018a; Claustre et al. 2020) and moored instruments (Bresnahan et al. 2014). There are examples of other chemical optodes including pH and pCO_2 (Chu et al. 2020), but historically they suffered from a lack of stability, sensitivity, or long response times (Fritzsche et al. 2018). However, recent

developments in pH optode technology have addressed many shortcomings, making it a potentially viable option for long term autonomous measurements.

There are several considerations for a successful pH optode: relevant pKa of the luminescent dye, immobilization of the dye to minimize loss of sensitivity and sensor drift, and resistance to photobleaching from measurements. In addition, it is desirable if the luminescence decay lifetime of the lumiphore is relatively long (in the microsecond range) as it enables robust measurements by the phase shift method adopted in optical oxygen sensors (Bittig et al. 2018a). Long luminescence lifetimes of the ruthenium and platinum lumiphores in oxygen optodes enables measurement of oxygen through a phase shift between the pulsed excitation signal and the luminescence emission signal (Bittig et al. 2018a). The phase shift is relatively immune to changes in excitation intensity resulting from drifts in the light source or emission intensity changes due to loss of the lumiphore through photobleaching. However, pH dependent lumiphores with long luminescence lifetimes appropriate for simple phase shift measurements have been difficult to develop (Wencel et al. 2014). The PyroScience Pico-pH sensor overcomes this limitation by using the dual lifetime referencing (DLR) technique (Klimant et al. 2001; Huber et al. 2001).

The DLR method enables phase shift measurements with relatively simple and low cost electronics and provides many of the benefits of a direct phase shift measurement, as in an oxygen optode. It measures the ratio of the phosphorescence of a reference dye (Egyptian Blue in this case) and the fluorescence of the pH sensitive dye. However, the sensor would remain sensitive to loss of the lumiphore over time. The pH sensitive lumiphore in the Pico-pH sensor absorbs and emits light in the red and near infrared (near-IR) region of the spectrum (Staudinger et al. 2019). These wavelengths greatly reduce the effects of photobleaching due to the low energy of the excitation radiation. The lumiphore is also covalently bonded to the support, which further reduces loss of the lumiphore over time. These properties contribute to greatly improved long term stability.

PyroScience distributes a self-contained data logger/transmitter (AquapHOx), as well as an OEM version of the pH sensor, the Pico-pH. We have purchased several Pico-pH devices and started initial characterization for sensor drift and their response to temperature and pressure (discussed below). Results from the Pico-pH should be directly applicable for the AquapHOx, as they use the same sensing element and driving electronics. Initially, the manufacturer was unwilling to provide us with the exact equation used to calculate pH from the analog signal dΦ (phase shift), as they considered this information proprietary. However, in a very recent correspondence with PyroScience (September 2022), they informed us that they are updating how they calculate pH and provided us with the exact form of the equation. They are currently in the beta stage of testing this update, and will release this information to the public shortly. The form of the equation is similar to that presented in Staudinger et al. 2019, but the main improvement in this update is that they utilize R (ratio of fluorescence of indicator dye to phosphorescence of reference compound) rather than the raw analog signal dΦ for pH calculations. This approach compensates for inter-sensor differences, as well as thermal effects on the sensor electronics, and is expected to provide more consistent and accurate pH measurements. The R parameter is included in the sensor output, and is expressed by the following equation:

$$R' = bottom' + \frac{top' - bottom'}{1 + 10^{\frac{pH - pka'}{slope'}}}$$

$$top' = top(1 + top_t(temp - 20)); \; bottom' = bottom(1 + bottom_t(temp - 20))$$

$$slope' = slope(1 + slope_t(temp - 20))$$

$$pKa' = pKa + pKa_t(temp - 20) - 0.5pKa_{is1}\left(\frac{\sqrt{\frac{20salinity}{1000}}}{1+\sqrt{\frac{20salinity}{1000}}} - 0.2791745 - pKa_{is2}\left(\frac{20salinity}{1000} - 0.15\right)\right)$$

Rearranging the above equations allows calculation of pH. While great strides were made to improve immobilization of the dye by covalently bonding the dye to the polymer substrate, there still is sensor drift due to loss of indicator to solution. The drift is temperature dependent (faster drift at higher temperatures), with a tendency toward higher pH. Because the source of the sensor aging drift is understood and unidirectional, it should at least partially predictable. PyroScience provides the following drift correction based on temperature and operating time (days in solution):

$$top_{n+1} = top_n e^{-d_{top}\Delta time};\ d_{top} = d0e^{-\frac{d1}{temp}}$$

$$bottom_{n+1} = bottom_n + d_{bottom}\Delta time;\ d_{bottom} = d2e^{-\frac{d3}{temp}}$$

At 20C, the drift is approximately 0.019 pH/mo. compared to 0.004 pH/mo. at 4C (typical of a profiling float park depth). While this level of drift would be considered unacceptable for most autonomous applications, it will be correctable if it is in fact repeatable and predictable as they claim. **Characterization of the Pico-pH sensor drift across multiple sensors and at different sustained operating temperatures is among the highest priority goals of the proposed research**

We have initiated three experiments at MBARI thus far. First, we are assessing the long term stability of the Pico-pH in the 1.5 million liter MBARI test tank by comparing sensor response to discrete pH measurements. Second, we are characterizing the pressure response of the sensor to 2000 dBar over a range of temperatures. Finally, we are establishing calibration protocols in our laboratory for these sensors that allows us to recreate and validate the calibration coefficients provided by the manufacturer. This will be essential to validate the best method to correct for sensor drift as well.

Preliminary data obtained with the Pico-pH sensor in the MBARI test tank show good performance when compared to discrete pH samples measured by spectrophotometry with purified mCP dye (Figure 3). The 10 m deep tank is normally at equilibrium with the atmosphere and has very stable pH, but the water level had been lowered 1 m for repairs and the tank was then refilled on June 1, 10 days before the start of our experiment. This drove the tank out of equilibrium with the atmosphere (makeup water comes from a deep ocean intake and has low pH) and created some initial stratification that was not recognized when discrete samples were taken. Discounting initial scatter due to the stratification, the sensor is tracking the discrete samples closely. pH optode data was calculated using an earlier version of the pH and drift equation provided by PyroScience, which only applied corrections to Top.

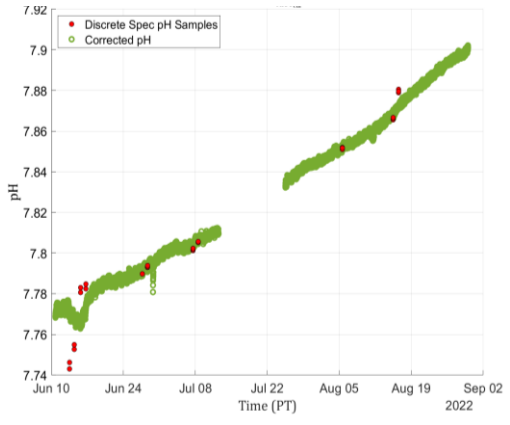


Figure 3: pH data from the MBARI test tank with the Pico-pH, compared to discrete samples (red dots)

Nonetheless, the good agreement between the sensor and discrete measurements is very encouraging, and suggests that sensor drift is repeatable and predictable.

The pH optode was temperature and pressure cycled in chambers that we utilize to calibrate DSDs. To determine the pressure coefficient of the sensor, sensor measurements must be made in a solution where pH is known over a range of temperature and pressure, and is within the sensing pH range of the optode (7-9). For this, we utilized equimolar tris buffer in artificial seawater (Tris buffer hereafter), as pH of this solution can be calculated as a function of temperature, salinity, (DelValls and Dickson 1998; Müller et al. 2018) and pressure (Rodriguez et al. 2015; Takeshita et al. 2017). Due to limited solution availability in the lab, we diluted the Tris buffer to salinity 7 for this experiment. Pressure cycles were conducted from 0 - 2000 dBar at 20, 10, and 2 °C, using the standard calibration routine used for DSDs. Sensor pH was calculated using factory calibration coefficients. We observed good agreement between the estimated solution and sensor pH at 1 atm, however, observed systematic errors over pressure (Figure 4). Specifically, sensor pH increased as pressure increased, whereas estimated solution pH decreased as pressure increased. This was after applying the pressure coefficient of -0.011 pH / 1000 dBar, provided by the manufacturer. This implies that the provided pressure coefficient is off by approximately a factor of 3, and is close to -0.033 pH / 1000 dBar. These preliminary experiments will be repeated with Tris buffer at salinity 35 over a temperature range of 2 to 35 °C. It is very encouraging though that the pressure effect is linear, and reproducible, with a small effect of temperature on the slope (Figure 4). The pressure sensitivity most likely arises from the change in pKa of the dye over pressure, and is explained by ΔV, or the change in partial molal volume of the dissociation reaction. This is supported by the fact that the pressure effect is linear, and has a slight temperature dependence (ΔV changes as a function of temperature). Since ΔV is a thermodynamic constant of the material, it should be consistent from sensor to sensor. This might alleviate the need to individually calibrate the sensors over pressure as currently done for the DSD. This will greatly simplify the production of pH sensors and reduce cost, although these results will need to be rigorously examined.

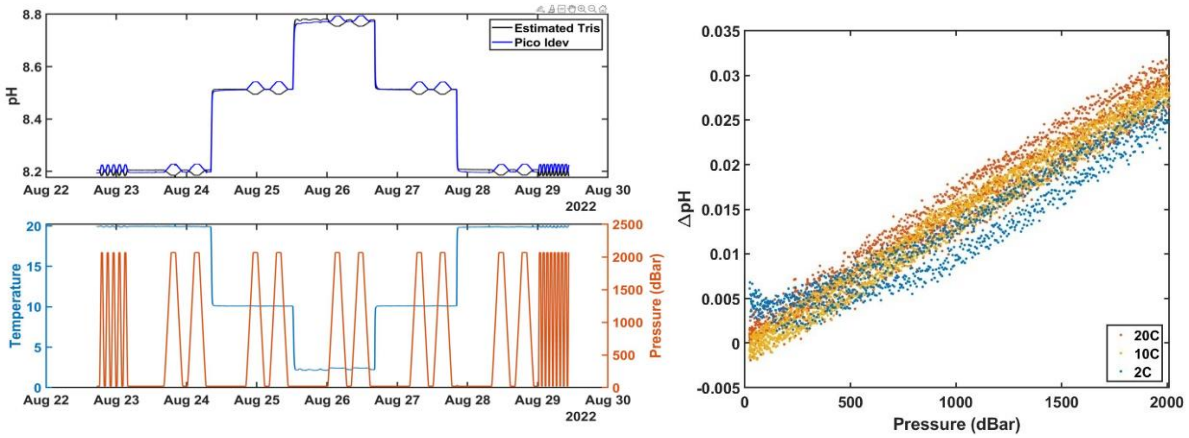


Figure 4: PT cycling results for the Pico-pH sensor.

Finally, we are establishing calibration protocols for the Pico-pH at MBARI and SIO. The calibration of the Pico-pH requires determining four coefficients: Top, Bottom, slope, and pKa. While pKa of the dye should be a thermodynamic constant, slight variations in synthesis and bonding of the dye to the polymer requires lot or sensor specific determination of the pKa. Each of these parameters has a temperature

coefficient, and in the case for pKa, has a salinity and pressure component as well. In the shift to mass production, Pico-pH utilizes a dye (and synthesis step) slightly modified from that published in Staudinger et al. 2019 (pers comm, C. Staudinger). Though similar to the published values, the properties of the new dye must be redetermined and published. Thus, thorough characterization and publication of the coefficients will be important. PyroScience has indicated that there are no plans to modify the dye in the future.

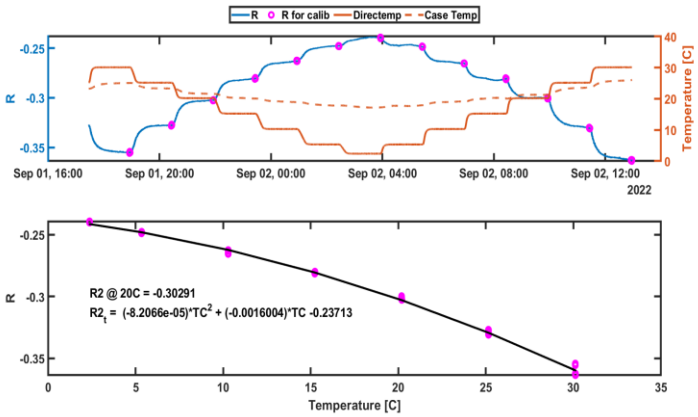


Figure 5: (top) Example data for Bottom calibration. (bottom) The Bottom dependence on temperature

The Top and Bottom coefficients can be determined by making measurements in a solution at low (~5) and high (~11) pH over a range of temperature, respectively. This is straightforward and currently being done in a temperature controlled jacketed beaker with either 0.1M citric acid or sodium carbonate (Figure 5). Once these coefficients are determined, then a sensor measurement in a solution near the pKa of the dye (~8) will constrain the slope and pKa. We are currently in the process of establishing this protocol by making simultaneous sensor and spectrophotometric pH measurements in the same solution. A well established and repeatable calibration protocol will be essential for validating manufacturer coefficients, as well as determining the best method to correct for sensor drift. Currently, from manufacturer recommendation, drift corrections are made to both Top and Bottom coefficients. Repeat calibrations of the same sensor will allow us to test this claim.

Alternative ISFET supplier

Developing an alternative ISFET based pH sensor is attractive, given the DSD's demonstrated ability for high performance and scalability in global observational networks (Newton et al. 2015; Claustre et al. 2020). Furthermore, there is a very promising solid state dual pH-TA sensor, based on the Honeywell ISFET, that is currently in the later stages of development (Briggs et al. 2017, 2020). Such a sensor could be transformative for oceanography. However, most commercially available ISFETs are not suitable for ocean observing. The Honeywell ISFET has several unique characteristics that enable high quality pH measurements in seawater: 1) Nernstian response (Takeshita et al. 2014) due to the use of a high buffer capacity insulating layer over the conduction channel; 2) electrical connections to the source, drain, and substrate channels on the back side of the chip that enables a robust mechanical encapsulation on the top side of the chip for high pressure applications; 3) large enough size (3 x 4 mm) to enable a mechanical encapsulation using an o-ring or gasket; and 4) an electronic driving circuit (referred to as the cap adapter circuit hereafter) that minimizes drift.

In particular, a Nernstian response (requirement 1) is essential for ocean pH sensing, as accurate pH measurements are required across all ranges of pH experienced in the ocean. The exact composition of the Honeywell ISFET gate material is proprietary. However, it is well documented that oxide materials with higher buffer capacity leads to better Nernstian response of the ISFET (Bergveld 2003; Sinha and Pal 2021).

In particular, Ta_2O_5 has a superior performance compared to its alternatives, such as SiO_2, Si_3N_4, or Al_2O_3. This difference is well supported by theory and results from a higher buffer capacity over the ISFET gate when Ta_2O_5 is utilized (Bergveld 2003). As a result, ISFETs with Ta_2O_5 gates consistently exhibit Nernstian or near-Nernstian response across multiple studies (Sinha and Pal 2021). This makes Ta_2O_5 gate material a requirement for an alternative ISFET. It is, however, a difficult material to work with in semiconductor fabrication facilities and not widely used.

We have identified two suppliers that manufacture ISFET chips that utilize Ta_2O_5 for their gate material: LioniX International (Netherlands) and Micropto (Italy). In particular, LioniX is a promising lead. They specialize in custom MEMS solutions, allowing us the flexibility to design the ISFET chip dimensions at a modest initial engineering cost. Their ISFET design incorporates electrostatic discharge protection, as does the Honeywell ISFET. This greatly reduces the possibility for damage to sensors during handling and operation. We have begun preliminary conversations with their engineering team, and thus far our interactions with them have been very encouraging. They are enthusiastic about this application, and have been very responsive to our inquiries. They have confirmed that multiple ISFET designs can be manufactured on a single wafer, which allows us to test multiple designs simultaneously, expediting the development effort. The cost of manufacturing a 10 cm diameter wafer is approximately 20K Euros, with an additional 7.5k Euros for engineering costs for custom ISFET layouts. A wafer takes approximately 5-6 months to complete after initial engineering efforts. We have purchased their evaluation kit (distributed by Microsens), which consists of a LioniX ISFET and AgCl reference electrode. However, no connection to the chip substrate was available in this configuration, thus could not use our cap adapter circuit to operate the ISFET. Given the cap adapter circuit is a key component for the DSD, we have decided to focus our efforts on engineering the alternative ISFET pH sensor rather than assess the performance of the evaluation board that utilizes a custom ISFET driving circuit by Microsens.

The LioniX ISFET, unfortunately, cannot be a drop-in replacement for the Honeywell ISFET for several reasons. First, the LioniX ISFET is an n-channel FET, while the Honeywell ISFET is a p-channel device. This requires a straightforward modification to the current cap adapter circuit, by reversing the polarity of the bias voltage applied across the source-drain channel. Modifications to the circuit design have been completed, and components are currently on order. Second and more importantly, the LioniX ISFET only provides top-side contacts for the source, drain, and substrate channels. A substantial engineering effort to redesign the pH sensor housing, is required to accommodate the top-side contacts. Historically, almost all ISFETs have top-side contacts, and were encapsulated using epoxy or resins (Oelßner et al. 2005), which is not a robust seal as fluid will inevitably penetrate between the ISFET surface and the resin, eventually leading to sensor failure. This is particularly true at high pressures. However, the flexibility to customize the size of the ISFET by LioniX provides an opportunity to improve the encapsulation and robustness of the pH sensor.

One of the challenges when developing the DSD was to design the mechanical seal on the ISFET surface based on the chip dimensions (3x4 mm), as Honeywell was not willing to alter its dimensions for our project. As a result, the seal was made on the face of the ISFET using a 0.02” diameter o-ring. This makes it inherently difficult to provide a robust seal because of the small surface area of the o-ring, and proper compression may not be applied onto the o-ring due to tolerance stack up of the various machined components involved in the sensor (e.g. housing and cover plate). We believe that the failure of this seal has been the main source of failure for the DSDs on profiling floats, leading to a mean lifetime of 2.5 years for these sensors on floats. Increasing the ISFET chip dimensions allows us to make a seal using a larger

o-ring or gasket, improving the robustness of the seal, thus the reliability of the overall sensor. This is because small variability in machining tolerances will have less impact on the overall integrity of the seal, along with more surface area to make the seal. We have updated the Deep-Sea-DuraFET design to utilize a gasket to make the seal over the ISFET to address this issue. This Gasketed DuraFet (GDF) design has shown good reliability on profiling floats thus far, but improved mean lifetime has not been demonstrated due to the limited number and longevity of sensors deployed on floats.

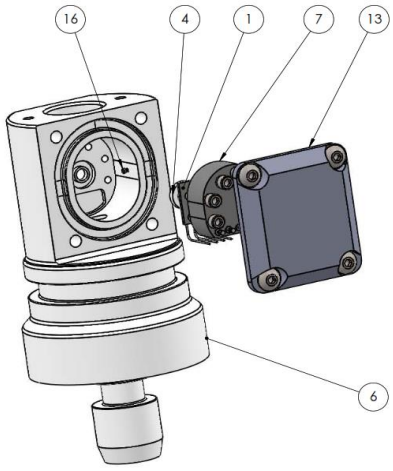


Figure 6: A high level concept drawing for the LioniX-pH sensor. The ISFET is labeled as 1. Reproduction of this drawing in part or whole without written permission of MBARI is prohibited.

Initial engineering efforts for the design of the ISFET pH sensor have begun. A high level concept drawing, based on our GDF design, is shown in Figure 6. This utilizes a substantially larger ISFET, approximately 5.5 mm x 7.6 mm, and has over double the surface area of the Honeywell ISFET. Connections to the source, drain, and substrate channels will be made via wire bonding (1mm diameter wires) on the top side of the ISFET, enabling a robust and secure electrical connection. To test various sealing methods (o-ring vs gasket) and wire bonding (e.g. wire size) approaches, we plan on including several configurations in the initial wafer. The details are currently in development, but we are planning to adjust chip size, source/drain channel dimensions, and electrical contact pad size and shape. The fully assembled sensor will be a drop-in replacement (mechanically) for the DSD on a profiling float to avoid any additional engineering efforts. The same reference electrode will be utilized as the DSD, as this has demonstrated to be robust. Therefore the equations to calculate pH should be identical to the DSD, thus, the same methods to calibrate the DSD will be utilized for the LioniX-pH sensor. Our group is in contact with E. Briggs at the University of Hawaii for the design of the ISFET to ensure the design meets the requirements for the dual pH-TA sensor (Briggs et al. 2017). Finally, this sensor should be easily adaptable for SeaFET/SeapHOx sensors (Bresnahan et al. 2014), and should lead to improved reliability from a more robust seal around the ISFET. We anticipate that the ISFETs will be delivered in early 2023, and laboratory and field deployments will follow.

We are coordinating with Seabird for this pH sensor design as well. MBARI is treating this as a new sensor development project, and a new non-disclosure agreement was signed between MBARI and SBS. We are sharing design ideas, and pursuing independent designs in parallel to accelerate the development process and to maximize chance of success. One key aspect of this new agreement is that any technology that will be licensed to SBS will not be an exclusive license, thus, the final ISFET design will be available for the community. This will prevent sole-source issues for pH sensor distribution, and increase competition to drive down sensor costs. The Cap Adapter circuit, though, will still be protected under the initial exclusive license for the DSD between MBARI, SBS, and Honeywell. However, we feel that there is enough information in the public domain about the Cap Adapter circuit that a skilled engineering team will be capable of reproducing the key aspects of this circuit, and/or improving its performance.

Laboratory and field performance characterization

The sensor performance will be characterized thoroughly in both the laboratory and in the field for both sensors. In the laboratory, sensors will be characterized for drift (and how to best correct for it), pH-dependent errors, temperature, pressure, and salinity effects on the sensor, and response time. Finally, performance of these sensors will be assessed in the field through deployments on coastal moorings, an underwater glider to 1000 m, and profiling floats for years.

Laboratory characterization: Long term sensor drift will be assessed through deployments in the MBARI and SIO test tanks for months to years, as currently being done for the Pico-pH (Figure 3). Discrete samples for spectrophotometric pH analysis using purified meta-Cresol Purple (mCP) will be collected periodically (Takeshita et al. 2021b), and compared to sensor measurements. Pico-pH will be recalibrated every ~3 months to determine which coefficients result in the drift (i.e. Top, Bottom, pKa, or slope). The LioniX pH sensor will be recalibrated every ~6 months to verify that k2 and fP (temperature and pressure coefficients) have not changed. This work will be conducted at MBARI and SIO.

Temperature and pressure effects on the sensor will be characterized using the pressure chambers currently used for DSD calibrations. The standard calibration routine for the DSD will be utilized for the LioniX pH sensor, and data will be processed using the operational calibration pipeline to determine k2 and fP (temperature and pressure coefficients). For the Pico-pH, we will first determine whether there are pressure effects on Top and Bottom by pressure cycling it in 0.1M Citric acid or Na_2CO_3 (n = 4 sensors). Then, we will conduct pressure cycles in Tris buffer with salinity 35 to obtain the ΔV of the dye between 2 and 30 °C (n = 4 sensors). We will assess how repeatable the pressure coefficient is for sensor to sensor, and if any pressure hysteresis exists. This work will be conducted at MBARI.

pH and salinity dependent errors will be determined following similar protocols outlined in Takeshita et al. 2014 and 2020. For pH dependent errors, we will make simultaneous pH measurements using spectrophotometry and the Pico-pH/LioniX in the same solution. Natural seawater will be used, and will be titrated from pH ~8.5 to ~7 using high-CO_2 seawater with over 100 discrete measurements throughout this range (Takeshita et al. 2020). Purified mCP will be used for spectrophotometry. This allows for detailed assessment of any pH dependent errors relative to the standard method for seawater pH analysis (Dickson et al. 2007; Liu et al. 2011). Salinity dependent errors will be assessed by diluting Tris buffer from salinity 35 to 5, and comparing the measured pH to calculated pH of the buffer solution (DelValls and Dickson 1998; Müller et al. 2018). Dilutions will be done at ~5 salinity increments, allowing us to also assess response time to large changes in salinity for these sensors, which would be useful for estuarine applications. Since the LioniX pH sensor will be using the same reference electrode as the DSD, we anticipate Nernstian response over the full salinity range (Takeshita et al. 2014). We anticipate small salinity effects on the Pico-pH, of around 0.03 from salinity 5-35, with larger effects at salinity below 15 (Staudinger et al. 2019). This work will be conducted at MBARI and SIO.

Response time of these sensors will be characterized at different temperatures using the pumped flow stream for profiling floats and gliders, with flow rates that are approximately 10 mL/sec. Experiments will be conducted in natural seawater. The sensor will first be thermally equilibrated with solution, and then solution pH will be changed in a stepwise fashion by addition of high or low CO_2 seawater. Once the solution is mixed thoroughly, the pump will be turned on, and the response time (T63, T90, and T95) will be quantified. The experiment will be repeated at temperatures 2C to 30 C at 5 C intervals. This work will be conducted at MBARI.

Field Characterization: Performance of these pH sensors will be assessed in the field in three different ways: moored deployments on coastal piers, underwater glider missions near Monterey Bay, and profiling floats. Hardware and software development for all three platforms are underway for the Pico-pH. Given that the LioniX ISFET pH sensor will be a drop-in replacement (mechanically) for the DSD, no additional development effort is anticipated for this sensor for field deployments. Glider and mooring deployments will be led by Takeshita and Martz, and profiling float deployments will be led by Johnson and Riser.

We propose to deploy Pico-pH and LioniX ISFET pH sensors alongside DuraFET pH sensors on two pier stations along the coast of California to assess their performance in situ. We will leverage ongoing shore station efforts to maintain SeapHOx sensors at the Monterey Wharf (Takeshita) and the SIO pier (Martz), funded by CeNCOOS and SCCOOS. Discrete samples for pH and total alkalinity are taken every several weeks at both stations, making them good sites to validate sensor drift. Furthermore, there is large temporal variability at these pier sites driven by local physics such as internal waves and bores (Takeshita et al. 2015; Hirsh et al. 2020), which allows assessment of dynamic response to pH and temperature of these sensors. We plan on collecting hourly samples over a tidal cycle on several occasions to assess the dynamic response of the sensors in situ. Custom data loggers that were designed for the Honeywell DuraFET (Hirsh et al. 2020) will be converted to incorporate the Pico-pH or LioniX-pH sensor. This is a straightforward engineering effort, and only requires modification to the top endcap, and design updates have been completed for the Pico-pH. The same controller can be utilized for these sensors, thus existing hardware will be utilized for this project. Fixed deployments alongside a rigorous discrete sampling regime will determine the viability of these sensors for the ocean acidification monitoring and coastal biogeochemistry community.

To assess performance on profiling platforms, the DSD and Pico-pH will be simultaneously operated on the Spray glider. This will allow direct comparison of the Pico-pH performance relative to the DSD. The DSD controller firmware has been updated to enable polling and powering the Pico-pH, and combines the pH data streams from the DSD and Pico-pH into a single output to the glider controller. A subset of the analog signal and diagnostic values will be sent back via satellite, and the full data will be downloaded upon recovery. Preliminary design for a neutrally buoyant Pico-pH housing has been completed (Figure 7). Housing material is Delrin with an OD of 1.25”, and a length of ~10” including the bulkhead and flow cell. This sensor will be plumbed into the pumped flow stream of the CTD, O_2, DSD, and fluorometer, which will allow faster sensor response and protection from sunlight contamination and degradation. Missions will be conducted near Monterey Bay as typically done through MBARI (Takeshita et al. 2021a), and measurements will be made on the descent and ascent to assess biases due to sensor response. We will leverage monthly time series cruises that make measurements for pH, TA, and DIC in the bay (Chavez et al. 2017) for validation (samples are currently analyzed in the Takeshita lab). Furthermore, we will conduct CTD casts to collect discrete samples alongside the glider at time of recovery

Figure 7: Schematic drawing of the Pico-pH sensor for glider application.

from our small boat RV Paragon, as is routinely done (Takeshita et al. 2021a). We propose to test two Pico-pH sensors on the Spray gliders over several missions. All data will be made publicly available in real time and QC'd through the gliderVIZ data portal (Takeshita et al. 2021a).

Deployment of these alternative pH sensors on profiling floats provide the best approach for assessing long-term performance on autonomous platforms. There are well established protocols for calculating and correcting sensor drift using reference pH fields at depth (Maurer et al. 2021) based on global empirical algorithms (Carter et al. 2018, 2021; Bittig et al. 2018b). Both pH sensors will be integrated onto APEX floats; sensors will be calibrated at MBARI and the floats will be assembled at UW. This approach has been successful for over 2 decades between these two institutions. Integration efforts for the Pico-pH are progressing well. Modifications to the APEX endcap is currently underway, and firmware development for the Pico-pH has been completed at UW, and is currently undergoing testing (~4 month process). The LioniX pH sensor will not require any hardware or software modifications, except for the update for the electronics to bias the ISFET, which is already complete. Therefore no additional engineering efforts are required to deploy LioniX pH sensors on APEX floats. Purchase of three APEX floats are included in this proposal for Pico-pH and O_2 sensors, as O_2 is a critical input for the empirical algorithm to assess sensor drift and performance. LioniX pH sensors will be deployed on GO-BGC or SOCCOM floats as no changes to the floats are required. We will leverage ongoing GO-BGC and SOCCOM activities for float deployment opportunities, and choose locations where there is a rich history of pH measurements such as HOT, BATS, or Station P to enable effective assessment of pH sensor performance.

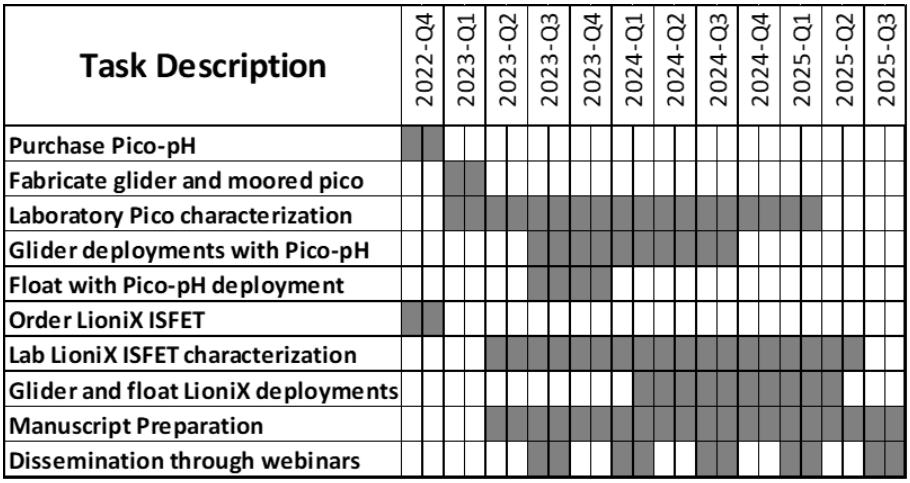
Broader Impacts

The main impact of this proposal is to rapidly develop an alternative pH sensor for the scientific community that is scalable for global ocean observational networks. The sudden announcement by Honeywell to discontinue the production of the ISFET chip will have immediate and severe impacts on our ability to observe the ocean. For example, NOAA funded projects alone purchase approximately 300 DuraFETs to support their programs, and they will all be impacted over months to a year. The full extent of projects that will be affected in the US (e.g. additional projects funded through NSF) and internationally is not known, but expected to be large. Furthermore, ocean Carbon Dioxide Removal (CDR) projects are rapidly gaining attention and philanthropic funding, and will likely start getting implemented on large scales in the near future. Thus, it is critical that we maintain the ability to effectively and economically monitor ocean CO_2 chemistry on local, regional, and global scales to accurately draw baselines and assess the impacts of these emerging CDR technologies. Global observational networks such as BGC-Argo and GOA-ON form the backbone for these capabilities, and relies heavily on DuraFET pH sensors to provide the critical CO_2 related measurements. This proposal will accelerate the ongoing development efforts by this team to provide a solution to this imminent problem. The two potential pH sensors included in this proposal are both capable of potentially filling most, if not all applications for DuraFET sensors, ranging from mesocosm, moored instrumentation, and autonomous profiling platforms.

Rapid and frequent dissemination of knowledge and experience gained from these new pH sensors will be critical for widespread use by the community. Therefore in addition to publishing our results in academic journals in a timely manner, we will host open webinars 2-3 times a year to update progress on this project. We will reach out to the Ocean Carbon and Biogeochemistry (OCB) program and ask if they would sponsor pH sensor update webinars to increase community attendance; initial conversations suggested they would be open to this. We will also add a session about pH sensor updates in the science workshop hosted by GO-BGC in 2023.

A goal of this project is to ensure that any sensors we develop or validate are widely available. We will work closely with essential industries such as Sea-Bird Scientific, PyroScience, LioniX and profiling float and glider manufacturers to ensure that they are aware of our work and able to contribute any suggestions towards manufacturability and reliability. Our team is already closely coordinating with most of these manufacturers through our preliminary development process. This should allow industry to rapidly adopt developed products from this project. Finally, we will avoid exclusive licenses with any manufacturer to promote competition and thus to drive down costs.

Timeline and anticipated deliverables is shown in the Gannt chart below.



***Qualification of Principal Investigators*:** The PI team is uniquely qualified for this project. They have a long history of successful and productive collaborations that have pioneered the efforts to develop DuraFET pH sensors that are now utilized for global observational networks such as BGC-Argo and the GOA-ON. For example, Johnson, Martz, and Riser led the development of the Deep-Sea-DuraFET pH sensor utilized on profiling floats, and Martz and Johnson led the development of the SeaFET and SeapHOx sensor packages. These technologies were all licensed to Seabird and made available to the community. Takeshita led the characterization of the DuraFET sensor, and the integration onto underwater gliders. All PIs are involved in the SOCCOM and/or GO-BGC projects, and Johnson is the director of GO-BGC, SOCCOM, and co-chair of BGC-Argo. Johnson, Martz, and Takeshita are experts in marine carbon dioxide chemistry and pH sensors, and are well poised to lead the development of the next generation of pH sensors for oceanography.

Prior NSF Support

NSF support for PI Takeshita: *Collaborative Research: Improving the accuracy and uncertainty associated with estimated pCO_2 from pH sensors on autonomous profiling platforms.* NSF OCE-2049117, $793,881to MBARI, 6/1/2021-5/31/2024. *Intellectual Merit*: DuraFET pH sensors on BGC-Argo provide an unprecedented opportunity to estimate surface pCO_2 across the global ocean to constrain air-sea CO_2 fluxes. This project aims to improve the utility of this powerful global dataset by rigorously assessing for systematic biases in estimated pCO_2 by quantifying pressure effects on key thermodynamic constants, assessing uncertainties in the calibration protocol for DuraFET sensors, and evaluating field pCO_2 estimates by comparing profiling DuraFET pH platforms to autonomous surface vehicles. *Broader Impacts*: Improved estimates for pCO_2 from BGC-Argo, thus, air-sea CO_2 fluxes will lead to better understanding of the global carbon cycle. For example, incorporation of this data into models could enable real-time carbon accounting on annual timescales. *Products & publications* resulting from this award include Carter et al. 2021.

NSF support for co-PI Johnson and co-PI Riser: Southern Ocean Carbon and Climate Observations and Modeling (SOCCOM and SOCCOM2), PI Jorge Sarmiento, Princeton (PLR-1425989, $22,381,623; renewed as OPP-1936222, $14,079,937), K. Johnson Subaward ($5,933,890) 9/1/2014 to 8/31/2020 and ($4,369,902) 9/1/2020 to 8/31/2025, S. Riser Subaward ($5,752,596) 9/1/2014 to 8/31/2020 and ($3,271,172) 9/1/2020 to 8/31/2025. *Intellectual Merit*: The SOCCOM team proposed to build and deploy ~200 BGC profiling floats in the Southern Ocean in SOCCOM and an additional 120 floats are being deployed in SOCCOM2. At this point, we have deployed over 220 floats since 2014, of which 111 are currently operating. A data system to process and quality control the observations has been developed at MBARI and all data are available to the public in real-time at the SOCCOM website and through the Argo data system. Shipboard measurements at the time of float deployment have been collected for nearly all floats and used to validate sensor operation. All shipboard data are available through the CCHDO website and the SOCCOM website. Over 160 peer-reviewed publications and 4 Ph.D. theses (number of others in progress) have been produced by SOCCOM scientists. Publications led by MBARI scientists include (Johnson et al. 2015, 2016, 2017a; b, 2022; Johnson and Claustre 2016; Takeshita et al. 2018b; Johnson and Bif 2021; Maurer et al. 2021). UW-led publications include (Drucker and Riser 2016; Hennon et al. 2016; Riser et al. 2016, 2018; Campbell et al. 2019; Wilson et al. 2019). *Broader Impacts*: A major role in outreach has been support of the SOCCOM Adopt-A-Float program, which has been led at MBARI. 153 floats have been adopted by schools in 39 states and 6 foreign countries. In addition, SOCCOM has contributed to the training and education of 15 postdocs (11 at least partially funded by SOCCOM), 14 graduate students (12 funded by SOCCOM), and 35 undergraduate students (8 of whom have received some SOCCOM funding) at five different institutions. 54% of these junior researchers have been female and ~9% have been participants from under-represented groups, with highest participation of under-represented groups at the undergraduate level.

NSF support for co-PI Martz: NSF Award OTIC 1155122 (PI: Todd Martz, SIO and co-PI: Andrew Kummel, UCSD), $659,543, *Development of an ISFET sensor for seawater Total Alkalinity and pH* (10/1/2012-9/30/2018) *Intellectual Merit*: The Martz lab at SIO developed a dual pH-A_T sensor utilizing solid state ISFET (ion sensitive field effect transistor) technology capable of rapid (<60 s) measurement of the aqueous carbon dioxide system ideal for autonomous platforms. Results indicate precision of 2-10 μmol kg^{-1} for A_T and 0.005 for pH which has a number of immediate applications for studying marine biogeochemical processes. *Broader Impacts* include development of a potentially transformative new technology for use by the ocean biogeochemistry community, in particular those studying calcium carbonate processes and ocean acidification. *Products & Publications* resulting from this award include Briggs et al., 2017 and Briggs et al., 2020.

NSF support for co-PI Gray: NSF OCE-1756882, $427,265, *Collaborative Research: Observations of Three-dimensional Transport Pathways and Biogeochemical Fluxes in the Southern Ocean using Autonomous Gliders*. 3/1/2018-2/28/2022. *Intellectual Merit:* We sampled around a BGC-Argo float in the Southwest Indian Ocean with two Seagliders, providing evidence for a hotspot of ventilation in a region of high eddy kinetic energy localized to a standing meander in the Southern. *Broader Impacts:* A postdoc, graduate student, and undergraduate received research training and novel observing strategies for multiple autonomous platforms were developed. *Products* include (Bushinsky et al. 2019b; Balwada et al. 2020, 2021; Dove et al. 2021, 2022)