Development of an integrated ISFET pH sensor for high pressure applications in the deep-sea

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LONG-TERM GOALS

The long-term goals of this project are to enable observations of pH in the ocean at depths to 2000 m using sensors deployed on autonomous platforms, particularly profiling floats of the type used in the Argo array. These systems will enable robust, basin-scale observations of changing pH driven by natural and anthropogenic processes.

OBJECTIVES

Develop a robust and stable pH sensor for deep-sea applications that is based on the Honeywell Durafet Ion Sensitive Field Effect Transistor (ISFET). The sensor should operate to depths of at least 2000 m. It should have a precision of ±0.001 pH and a stability of 0.005 pH over periods up to 5 years throughout the oceanic temperature and salinity range. Capabilities will be demonstrated with deployments on four Webb Research Apex profiling floats.

APPROACH

Our laboratory experiments (Martz et al., 2010) have shown that the Honeywell Durafet pH sensor has the stability, precision and speed needed for long-term (year or more), in situ pH measurements in the ocean. However, the commercially available version of the Durafet is only rated to operate at maximum pressures equivalent to a depth of around 70 meters. We are, therefore, adapting the sensor to operate at high pressure. This requires repackaging the ISFET die in a rigid support structure with a proprietary process used to isolate the ISFET die substrate from solution, while still exposing the ISFET gate to the solution. Secondly, we are developing a pressure tolerant reference electrode that is stable and has a rapid response rate. Finally, we have constructed a temperature and pressure controlled facility that allows the sensor to be tested and calibrated throughout its operating range.

WORK COMPLETED

We have made significant progress towards our objective of developing a stable, pressure tolerant pH sensor that can be deployed on profiling floats. Our focus in 2010 was developing the fundamental infrastructure needed to test pH sensors at high pressure and we then began the process of developing pressure tolerant pH sensors. During 2011, we continued designing, testing and refining high pressure pH sensors based on the Honeywell Durafet ISFET die. A number of prototype pH and reference sensor designs were developed at Honeywell and at MBARI. These designs have been tested in the laboratory high pressure test facility in order to optimize the sensor design. That work culminated in the development of a prototype pH sensor capable of deployment in the ocean. That sensor has now been deployed multiple times to a depth of 1000 m on cruises offshore California. In addition to this work, an electronic controller capable of deployment in a profiling float was developed in 2010 and fully tested and debugged in 2011. During 2012, the first profiling floats with Deep-Sea Durafet pH sensors were built and deployed at the Hawaii Ocean Time-series (HOT) station ALOHA. The data returned by these systems appears to meet or exceed all of our objectives.

RESULTS

Our major result in 2012 is deployment of the Deep-Sea Durafet on a Teledyne/Webb Research Apex profiling float. This float was deployed at HOT station ALOHA (Fig. 1). It should operate for five years with vertical profiles at five day intervals from 1700 m depth to the surface. In addition, the Deep-Sea Durafet pH sensor was deployed on a CTD/Rosette system on a research cruise off Southern California.

The results (Fig. 1 and Fig. 2) show that the sensor can return very high quality pH measurements that have an absolute calibration based on laboratory measurements that are traceable to well defined standards. This is an oceanographic first. It has not previously been possible to calibrate an oceanographic pH sensor in the lab and then make absolute measurements in the ocean through large pressure and temperature changes due to shifts in sensor calibration. We believe that this sensor will greatly increase our ability to observe changing pH in the ocean. Measurements in the upper ocean suggest that sensor precision is comparable to the annual pH change due to ocean acidification (Fig. 2). An array of profiling floats equipped with pH sensors would be capable of directly monitoring the process of ocean acidification.

Further refinement of the sensor is continuing. We are working towards a design that will have a much more reproducible pressure coefficient. In order to enable a more stable design, our partners at Honeywell are implementing a highly integrated unit.

IMPACT AND APPLICATIONS

Economic Development

Development of a robust, accurate pH sensor that operates at high pressure will have a broad range of economic impacts that range from industrial process control, carbon storage in geological formations and carbon storage in the ocean. This is in addition to the benefit obtained from direct observations of ocean pH.

Quality of Life

The high pressure pH sensor will have direct applications to our understanding of ocean acidification and the impacts on ecosystem processes and associated economic impacts. This is a non-trivial issue for the population of South Pacific island nations, where coral atolls form the geological base for their cities.

TRANSITIONS

Economic Development

It is our intent to develop a commercially available product for ocean observations. Our partners are currently conducting a marketing study to understand the potential implications of a robust, accurate, and pressure tolerant pH sensor in other areas.

Quality of Life

Our project will enable widely distributed observations to be made throughout the ocean interior. Such a capability would allow an observing system for ocean acidification to be developed.

RELATED PROJECTS

The overarching goal of our research is to enable global scale observing of biogeochemical properties. Related projects include the NOPP project (N00014-09-10052) to develop a commercial version of the ISUS (In situ ultraviolet spectrophotometer) for the Apex profiling float. An NSF funded project (NSF 0825348, Collaborative Research: In situ measurements of oxygen and nitrate with profiling floats deployed at ocean time-series stations) is focused on making time series observations near open ocean time-series sites near Hawaii, Bermuda, the Gulf of Alaska and in the Southern Ocean. This project will benefit when the pH sensor becomes available.

REFERENCES

Martz, T. R., J. G. Connery and K. S. Johnson. 2010. Testing the Honeywell Durafet® for seawater pH applications. Limnology and Oceanography: Methods, 8, 172-184.

Fig. 1. First 18 vertical profiles of pH measured by profiling float 7672, which was deployed at the Hawaii Ocean Time-series (HOT) station, are shown in blue. Measurements of pH made by HOT personnel on water samples collected on monthly cruises from 2008 to 2010 are shown in red.

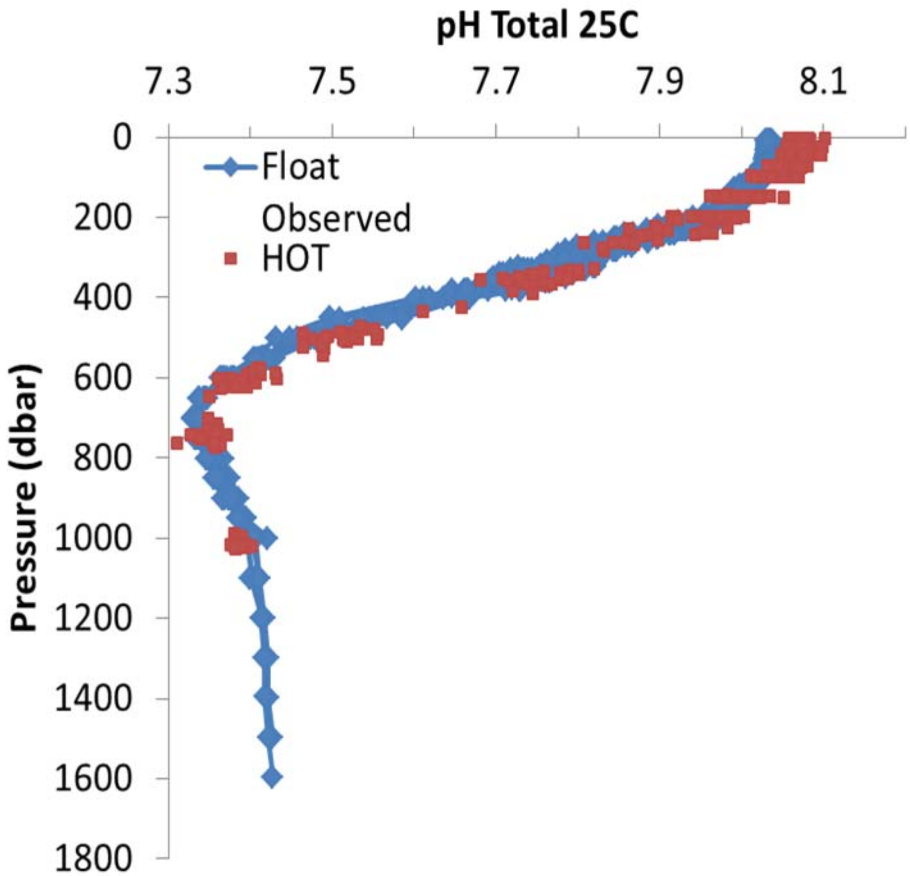

Fig. 2. pH values measured with the Deep-Sea Durafet mounted on a CTD/rosette sampler (solid lines) and pH values measured spectrophotometrically using m-cresol purple indicator in samples collected with the rosette (dots) at four stations off Southern California. Measurements made by Todd Martz and Yui Takeshita (SIO).

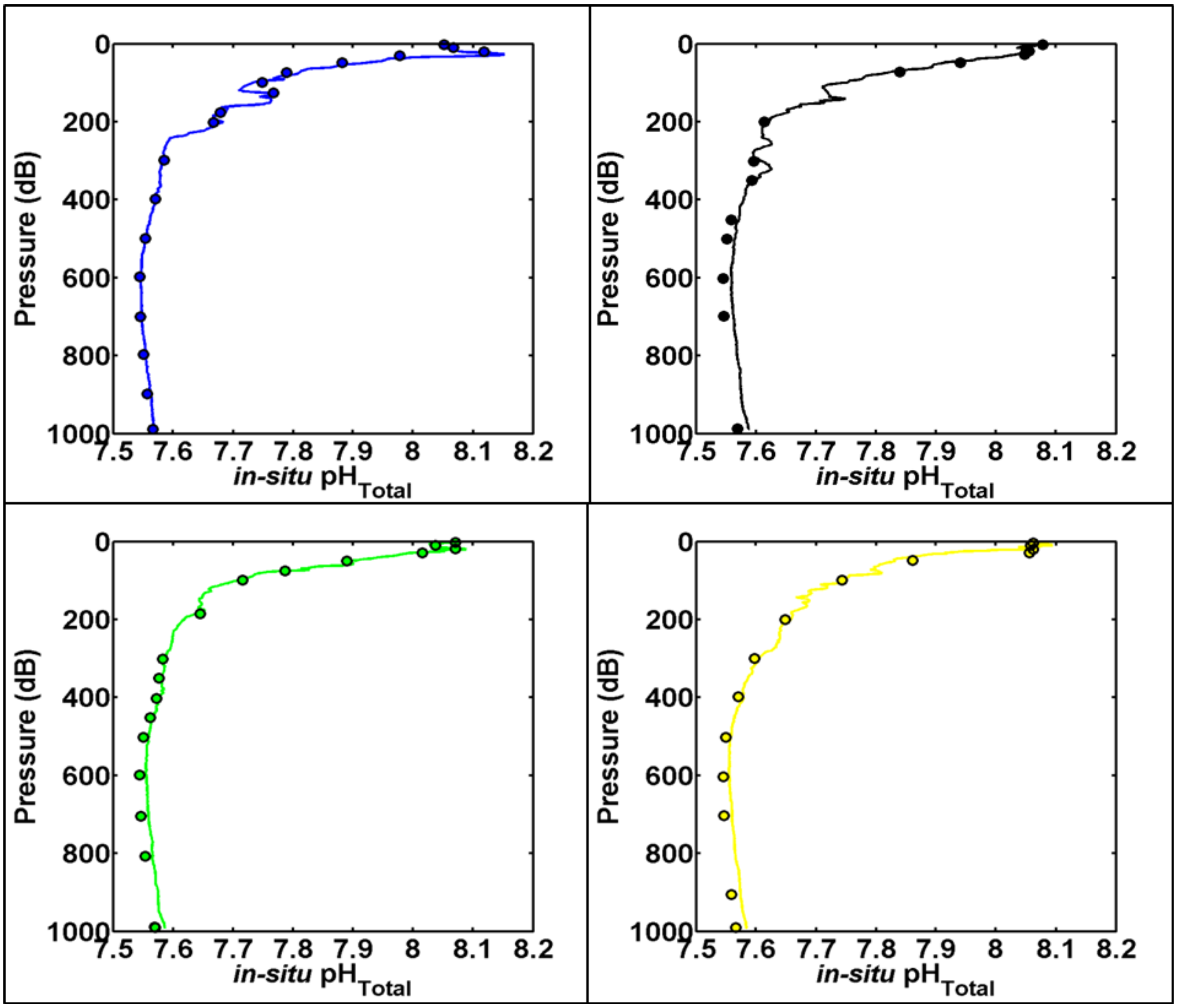

Fig. 3. pH in the upper 150 m of the water column on the first 8 profiles of float 7672. One standard deviation of the pH measured in the mixed layer (upper 50 m) is 0.0015 pH, which is comparable to the annual pH change due to ocean acidification (-0.0017 pH/year).